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PROCEEDINGS OF THE THIRTIETH ANNUAL CONVENTION.

NOVEMBER 1913.

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CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS AS AMENDED AND ADOPTED NOVEMBER 18, 1914.

(1) This association shall be known as the Association of Official Agricultural Chemists of North America. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle food, dairy products, human foods, medicinal plants, drugs, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State, provincial, or national agricultural experiment station or agricultural college, or with any State, provincial, or national institution or body in North America charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Analytical chemists connected with municipal laboratories that perform work upon any of the subjects specified in Paragraph (1) hereof, shall be entitled ex officio to associate membership, with the privilege of discussion, but without the privileges of entering motions, voting or becoming eligible for office. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers or involving definitions, nomenclature, laws, or regulations relating to fertilizers. Only such chemists as are connected with institutions exercising official cattle-food control shall vote on questions involving methods of analyzing cattle foods or involving nomenclature, definitions, laws, or regulations relating to cattle foods. Only such chemists as are connected with institutions exercising official food or drug control shall vote on questions involving methods of analyzing food or drugs or involving nomenclature, definitions, laws, or regulations relating to food or drugs. All persons eligible to membership shall become members ex officio and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice president, and a secretary, who shall also act as treasurer, and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, from among the members of the association, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate. [Construed by resolution passed in 1911 to mean the outgoing executive committee; standing rule adopted that the committee consult with each referee in the appointment of associates.]

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish

blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive commitee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

By-Laws.

(1) Any amendment to these by-laws or additions thereto may be proposed at a meeting of the association and shall be published in the Proceedings. It may then be adopted by a majority vote of the association at the next meeting.

(2) These by-laws or any portion of them may be suspended without previous notice by a unanimous vote of those present at any meeting of the association.

(3) There shall be a committee of nine members which shall be designated as the committee on recommendations of referees. The president shall appoint three members of this committee to serve six years, such appointments to be made every other year as the terms expire. The chairman of the committee shall be appointed by the president and shall divide the nine members into three subcommittees (A, B, and C), and shall assign to each subcommittee the reports and subjects it shall consider.

(4) Each referee shall forward to the chairman of the committee on recommendations at least three weeks before the meeting of the association his recommendations and a sufficient abstract of his report to enable the committee to act intelligently on the recommendations.

As soon as possible after the annual meeting of the association each retiring referee shall transmit a copy of his report and recommendations, together with a statement of the action taken by the association upon the same, to the referee for the next year. [1911.]

(5) A method shall not be adopted as provisional or a provisional method amended until such method or amendment has been reported by the appropriate referee and published in the Proceedings of the association.

(6) A method shall not be adopted as official or an official method amended until such method or amendment has been recommended as official for at least two years by the appropriate referee.

(7) Each college, experiment station, bureau, board, or other institution entitled to representation in the association shall contribute annually $2, and its representatives shall not be qualified to vote or hold office in the association unless such annual dues have been paid, but these shall not be cumulative.

PROCEEDINGS OF THE THIRTIETH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1913.

FIRST DAY.

MONDAY—MORNING SESSION.

The thirtieth annual convention of the Association of Official Agricultural Chemists was called to order by the president, G. S. Fraps, of College Station, Texas, on the morning of November 17, 1913, at the Raleigh Hotel, Washington, D. C. The following members and visitors were present:

MEMBERS AND VISITORS PRESENT.

Adams, A. B., Bureau of Internal Revenue, Washington, D. C.
Adams, A. C., Maryland Agricultural College, College Park, Md.
Adams, G. H., 88 Broad Street, Boston, Mass.
Albright, A. R., Bureau of Chemistry, Washington, D. C.
Allen, W. M., Department of Agriculture, Raleigh, N. C.
Almy, L. H., Bureau of Chemistry, Washington, D. C.
Alsberg, C. L., Bureau of Chemistry, Washington, D. C.
Ames, J. W., Agricultural Experiment Station, Wooster, Ohio.
Andrews, L. W., Bureau of Chemistry, Washington, D. C.
Averitt, S. D., Agricultural Experiment Station, Lexington, Ky.

Bacon, C. B., Bureau of Chemistry, Washington, D. C.
Bailey, E. M., Agricultural Experiment Station, New Haven, Conn.
Bailey, H. S., Bureau of Chemistry, Washington, D. C.
Bailey, L. H., Bureau of Chemistry, Washington, D. C.
Baker, E. L., Agricultural Experiment Station, Geneva, N. Y.
Baker, H. A., 52 East Forty-first Street. New York, N. Y.
Balls, A. K., Bureau of Chemistry, Washington, D. C.
Barr, J. A., Exposition Building, San Francisco, Calif.
Bartlett, G. M., Joseph Campbell Co., Camden, N. J.
Bartlett, J. M., Agricultural Experiment Station, Orono, Me.
Bartow, Edward, State Water Survey, Urbana, Ill.
Bates, Carleton, Bureau of Chemistry, Washington, D. C.
Baughman, W. F., Bureau of Chemistry, Washington, D. C.
Beyer, G. F., Bureau of Internal Revenue, Washington, D. C.
Bidwell, G. L., Bureau of Chemistry, Washington, D. C.
Biesterfeld, C. H., Bureau of Chemistry, Washington, D. C.

Bigelow, W. D., National Canners Association, Washington, D. C.
Billings, G. A., Bureau of Plant Industry, Washington, D. C.
Bisbee, D. B., Food and Drug Inspection Laboratory, St. Louis, Mo.
Bishop, H. E., State Board of Health, Indianapolis, Ind.
Bitting, A. W., National Canners Association, Washington, D. C.
Bitting, Katherine G., National Canners Association, Washington, D. C.
Black, C. L., Bureau of Chemistry, Washington, D. C.
Blair, A. W., Agricultural Experiment Station, New Brunswick, N. J.
Blum, Wm., Bureau of Standards, Washington, D. C.
Boughton, E. W., Bureau of Chemistry, Washington, D. C.
Bower, J. H., Bureau of Chemistry, Washington, D. C.
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Cameron, F. K., Bureau of Soils, Washington, D. C.
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REPORT ON PHOSPHORIC ACID.

By A. J. Patten, *Referee*, and L. S. Walker, *Associate Referee.*

The referee on phosphoric acid has been guided in his work of the past year by the recommendation made by the referee for 1912, that further work be done on the methods for basic slags with the methods and slags used by that referee. About 50 pounds of each of the three slags used last year were received from the referee for 1912 soon after the last association meeting. Uniform samples were prepared and sent to twelve laboratories early in December, 1912, and more samples to ten other laboratories early in January, 1913. Reports have been received from twenty-three chemists in seventeen laboratories. Special attention has been given to the purity of the magnesia precipitates and each collaborator was asked to test all precipitates after ignition and weighing for the presence of iron and silica.

The following instructions were sent out with the samples:

INSTRUCTIONS FOR COOPERATIVE WORK ON BASIC SLAG.

Dear Sir: There are being sent to you, under separate cover, three samples of basic slag phosphate. Please have them analyzed by the methods outlined below:

1. Determine moisture at 100° C.

2. Determine total phosphoric acid on each by the official gravimetric method.

(A) Using (a_4) method of making solution (See Bur. Chem. Bul. 107, Rev., p. 2).

(B) Using (a_7) method of making solution (See Bur. Chem. Bul. 107, Rev., p. 2).

(a) Dehydrate an aliquot of solutions (a_7) by evaporating to dryness on a steam or hot water bath; take up with 5 cc. of hydrochloric acid and 25 cc. of warm water; digest to complete the solution and filter off the silica (SiO_2); wash six times with hot water. Determine phosphoric acid in solutions by the official gravimetric method.

(b) Determine phosphoric acid in an aliquot of solutions (a_7) by the optional volumetric method (See Bur. Chem. Bul. 107, Rev., p. 4 (b)).

3. Determine available phosphoric acid as follows:

(A) *Making citric solution.*—Weigh 5 grams of the basic slag, transfer to a one-half liter Wagner flask containing 5 cc. of 95 per cent alcohol. The flask should have a neck width of at least 20 mm. and be marked at least 8 cm. below the mouth. Make up to the mark with dilute citric acid solution (2 per cent) of a temperature of 17.5° C. Fit the flask with a rubber stopper and put at once into the rotary apparatus for 30 minutes, making 30 to 40 revolutions per minute. Take off and filter immediately.

(B) *Analysis of citric solution.*—As soon as the filtration is completed, analyze the solution at once according to the following methods:

(a) *Molybdate method* (provisionally adopted 1911).—To 50 cc. of the clear filtrate add 100 cc. of molybdate solution made according to the official methods. Put the beaker into a water bath until the temperature reaches 65° C.; take out and allow to cool at ordinary temperature. Then filter and wash the yellow precipitate of phosphomolybdate of ammonia four or five times with 1 per cent nitric acid. Dissolve in 100 cc. of 2 per cent ammonium hydroxid (cold), nearly neutralize with hydrochloric acid, and add to the solution 15 cc. of magnesia mixture (made according to the official method) drop by drop during continuous stirring. After 15 minutes

add 10 to 12 cc. of ammonium hydroxid solution (specific gravity 0.90), then cover the beaker with a glass cover and allow to stand for about 2 hours. Filter the double phosphate of ammonia and magnesia through a tared platinum Gooch crucible, wash six times with 2 per cent ammonium hydroxid, dry, and proceed as customary for phosphoric acid determinations.

(b) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of the clear solutions by the optional volumetric method. (See Bur. Chem. Bul. 107, Rev., p. 4, (b)).

(c) *Citrate of ammonia magnesia mixture method.*—Place 100 cc. of the clear filtrate into a 200 cc. flask and add 50 cc. of citrate magnesia mixture (made by placing 200 grams of citric acid and 40 grams of ammonium chlorid in a liter flask, adding 200 cc. of water and 500 cc. of ammonium hydroxid (20 per cent), keeping the flask stoppered until the contents are dissolved and cooled down, then adding 55 grams of chlorid of magnesia and filling up to the mark with water). Heat the flask slightly (about 15 minutes) by means of a Bunsen burner turned low, until the silica (SiO_2) has been precipitated. Shake the flask in order to conglomerate the precipitate, and continue heating to the boiling point. Allow to cool, add 25 cc. of hydrochloric acid (specific gravity 1.124) and allow it to stand about 30 minutes with occasional shaking. Fill up to the mark with water, insert rubber stopper in flask, and shake vigorously several times until the silica (SiO_2) precipitate has been divided into very fine particles. Filter and to 100 cc. of the filtrate (0.5 gram of basic slag) add 50 cc. of a 10 per cent solution of ammonium hydroxid while stirring the contents of the beaker. Continue stirring, preferably by means of a stirring apparatus, for 30 minutes, filter the precipitate, and treat as usual.

PREPARATION OF SOLUTIONS.

1. *Concentrated solution of citric acid (10 per cent).*—Dissolve in water exactly 200 grams of chemically pure crystallized citric acid having its full percentage of water of crystallization. Make up this solution to exactly 2 liters. (When a large number of analyses are to be made, 0.5 gram of salicylic acid should be added to the liter of this solution to prevent decomposition.)

2. *Dilute solution of citric acid (2 per cent).*—Mix exactly 1 volume of the concentrated citric acid solution with 4 volumes of water. The resulting solution should have a temperature of about 17.5° C. when used.

PRECAUTIONS AND FURTHER INFORMATION.

1. A photograph and detailed drawings of an inexpensive but efficient shaking apparatus were sent out by the referee for 1911. A copy will be forwarded, on request, to anyone coöperating in the work this year.

2. Ordinary shaking or rocker apparatus must not be substituted for the rotary apparatus prescribed for shaking the flask, as they differ in construction and effect; the rotary apparatus must turn round its axle 30 to 40 times per minute. Variation within these limits has no marked influence on the results.

3. The half-liter flasks (after the design of Wagner) must have a neck width of at least 20 mm. and are marked at least 8 cm. below the mouth. These two points are important, since if the neck width is too narrow and the mark too high, the result will be too low, owing to the movement of the liquid being so limited. (The proper flasks are listed in E. and A. Catalogue, see No. 4589a.)

4. The filtration must be done immediately after 30 minutes' rotation, and it is recommended to use a folded filter paper of such size that the whole quantity of liquid can be poured into the filter at once. Small and bad filtering papers give

rise to error, in consequence of too slow filtration. If at first the filtrate is not clear, it must be filtered again (through the same filter) until it becomes clear.

5. After filtering the citric solution of the basic slag, the precipitation of the phosphoric acid should be carried along without delay, as long standing increases the tendency of the silica to precipitate during the operation.

6. If the beaker containing the mixture of phosphatic and molybdic solutions is put into the water bath until the temperature reaches between 60° and 70°C., a precipitate free from silicic acid results. If heating is continued for a considerably longer period of time, the precipitate will often be mixed with silicic acid, especially when the molybdic solution is not added to the filtrate immediately but only after 6 to 12 hours (or longer) after filtration. If silicic acid is present the precipitate dissolves slowly in ammonium hydroxid, but at first not clearly. Special attention must be paid to the point that the yellow precipitate is dissolved quickly and quite clearly by ammonium hydroxid (2 per cent) not made warm. If the solution becomes clear only after some time, molybdic solution and nitric acid must be added to same in order to get a pure precipitate of phosphomolybdate of ammonia; in other words, the phosphoric acid must be reprecipitated by the molybdic solution.

7. Since the presence of iron and silica has been noted in the magnesia precipitate it is recommended that these substances be tested for in all magnesia precipitates after ignition. This point is important and every coöperator is urged to give it special attention.

Please return results to the referee not later than February 1, 1913.

RESULTS OF COLLABORATION ON BASIC SLAG.

Phosphoric acid in Sample 1.

ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID				AVAILABLE PHOSPHORIC ACID		
		Gravimetric method using (a_4)	Gravimetric method using (a_7)	Gravimetric method using (a_7) dehydrated	Volumetric method using (a_7)	Molybdate method	Volumetric method	Citrate of ammonia magnesia mixture method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A. J. Patten, East Lansing, Mich.	....	[1]18.89	18.65	18.01	18.23	15.38	14.64	15.14
W. C. Marti, East Lansing, Mich.	0.23	18.47	18.74	18.53	18.23	14.53	14.70	14.65
A. K. Hart, East Lansing, Mich.	0.15	18.37	18.30	18.30	18.22	14.78	14.47	14.90
P. L. Hibbard, Berkeley, Calif.	....	18.36	[1]19.43	[1]19.50	18.20	[1]16.10	[1]16.50	[1]16.50
W. H. Dore, Berkeley, Calif.	0.19	[1]18.93	18.41	18.74	18.14	15.71	[1]16.65	[1]16.22
L. S. Walker, Amherst, Mass.	0.19	18.41	18.69	18.33	18.18	15.19	15.11	15.40
B. D. Wilson, Lexington, Ky.	0.12	18.45	18.24	.....	18.18	15.02	15.06	15.07
E. E. Sawyer, Orono, Me.	....	[1]19.28	[1]18.89	18.41	.....	15.25	.....	14.72
J. C. Jurrjens, Madison, Wis.	0.17	18.24	18.21	.....	.....	.....	.....	.....
B. E. Curry, Durham, N. H.	0.12	[1]19.87	[1]19.81	[1]19.61	[1]19.93	14.94	[1]16.45	14.53
Benj. Freeman, Clemson College, S. C.	0.23	17.89	[1]17.45	18.10	17.93	14.53	14.45	14.69
E. G. Proulx, La Fayette, Ind.	0.33	18.15	18.18	.....	18.12	14.77	14.83	14.69
W. B. Ellett, Blacksburg, Va.	....	18.40	18.18	18.15	.....	14.82	.....	.....
H. H. Hill, Blacksburg, Va.	0.06	18.30	18.36	[1]18.87	.....	14.64	.....	.....
M. I. Watkins, Columbia, Mo.	0.17	[1]19.11	18.47	.....	[1]17.83	15.68	[1]11.26	15.08
M. L. Lowry, Columbia, Mo.	....	.....	.....	.....	.....	.....	14.31	.....
J. R. Tucker, Fayetteville, Ark.	0.25	18.09	18.64	18.66	18.10	14.08	15.48	[1]17.34

[1] Not included in average.

Phosphoric acid in Sample 1—Continued.

ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID				AVAILABLE PHOSPHORIC ACID		
		Gravimetric method using (a_4)	Gravimetric method using (a_7)	Gravimetric method using (a_7), dehydrated	Volumetric method using (a_7)	Molybdate method	Volumetric method	Citrate of ammonia magnesia mixture method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A. K. Burke, Geneva, N. Y.	0.15	18.61	18.25	18.53	18.27	14.91	15.20	15.06
H. D. Edmiston, State College, Pa.	0.12	18.59	18.63	18.50	.....	14.56	.....	14.26
Paul Rudnick, W. L. Latshaw, Chicago, Ill.	....	18.45	.....	18.26	18.46	15.32	15.54	15.67
L. B. Broughton, College Park, Md.	....	18.37	[1]19.20	18.26	.....	15.50	.....	15.71
A. C. Adams, College Park, Md.	....	18.15	18.12	17.95	.....	.....	.....	.....
S. H. Wilson, Atlanta, Ga.	0.21	18.05	18.10	18.00	17.90	14.10	14.06	14.88
Average	0.18	18.32	18.39	18.31	18.17	14.93	14.82	14.96

[1] Not included in average.

Phosphoric acid in Sample 2.

A. J. Patten	....	17.41	17.25	16.86	16.77	15.43	14.72	15.32
W. C. Marti	0.38	17.06	17.33	17.01	16.85	14.69	14.85	14.79
A. K. Hart	0.26	16.96	16.66	16.70	16.43	15.06	14.66	15.11
P. L. Hibbard	....	17.37	17.03	[1]17.99	16.90	15.79	[1]16.30	[1]16.10
W. H. Dore	0.30	17.31	17.02	17.52	17.04	15.96	[1]16.30	15.90
L. S. Walker	0.24	17.42	17.06	17.03	16.74	15.26	15.15	15.46
B. D. Wilson	0.21	16.84	16.62	.....	16.65	14.89	15.04	14.96
E. E. Sawyer	....	17.59	17.34	17.29	.....	14.98	.....	15.44
J. C. Jurrjens	0.34	16.42	17.09	.....	.....	.....	.....	.....
B. E. Curry	0.20	[1]17.72	[1]17.60	17.35	[1]18.58	15.08	[1]16.67	14.49
Benj. Freeman	0.30	16.61	16.87	[1]16.20	16.35	14.72	14.80	14.82
E. G. Proulx	0.33	16.73	16.69	.....	16.61	14.55	14.93	14.63
W. B. Ellett	....	16.43	16.78	16.82	.....	14.88	.....	.....
H. H. Hill	0.17	16.96	16.98	17.18	.....	15.13	.....	.....
M. I. Watkins	0.23	17.41	16.97	.....	16.35	15.70	[1]10.84	15.19
M. L. Lowry	....	.....	.....	.....	.....	.....	14.44	.....
J. R. Tucker	0.28	16.99	16.81	16.78	16.55	14.88	15.28	14.86
A. K. Burke	0.22	16.88	16.94	17.19	16.80	14.65	15.33	15.17
H. D. Edmiston	0.21	17.11	16.81	16.88	.....	14.42	.....	14.45
Paul Rudnick, W. L. Latshaw	....	17.23	.....	16.72	17.08	15.37	15.59	15.46
L. B. Broughton	....	17.20	17.52	17.31	.....	15.90	.....	[1]16.21
S. C. Adams	....	16.79	16.87	16.68	.....	.....	.....	.....
S. H. Wilson	0.26	16.64	16.72	16.56	16.40	14.16	14.02	14.94
Average	0.26	17.02	16.97	16.99	16.68	15.08	14.90	15.06

[1] Not included in average.

Phosphoric acid in Sample 3.

ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID: Gravimetric method using (a_4)	TOTAL PHOSPHORIC ACID: Gravimetric method using (a_7)	TOTAL PHOSPHORIC ACID: Gravimetric method using (a_7) dehydrated	TOTAL PHOSPHORIC ACID: Volumetric method using (a_7)	AVAILABLE PHOSPHORIC ACID: Molybdate method	AVAILABLE PHOSPHORIC ACID: Volumetric method	AVAILABLE PHOSPHORIC ACID: Citrate of ammonia magnesia mixture method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A. J. Patten	....	14.90	14.77	14.43	14.32	13.43	12.84	13.27
W. C. Marti	0.47	14.61	14.88	14.50	14.45	12.95	12.93	12.95
A. K. Hart	0.35	14.48	14.43	14.46	14.28	13.31	12.86	13.38
P. L. Hibbard	....	14.88	14.75	15.33	14.75	13.49	13.70	13.56
W. H. Dore	0.33	15.02	14.62	15.20	14.50	13.53	13.80	13.46
L. S. Walker	0.34	14.81	14.82	14.87	14.45	13.17	13.07	13.28
B. D. Wilson	0.22	14.72	14.35	.....	14.56	13.26	13.05	13.09
E. E. Sawyer	....	15.52	14.71	15.23	.....	13.14	.....	13.65
J. C. Jurrjens	0.48	14.35	[1]13.05	.....	.....	.....	.....	.....
B. E. Curry	0.25	[1]16.37	15.11	15.07	[1]16.07	13.07	[1]14.57	12.52
Benj. Freeman	0.30	14.32	14.06	14.67	14.50	12.69	12.75	12.82
E. G. Proulx	0.42	14.19	14.27	.....	14.22	[1]11.94	[1]11.98	[1]11.89
W. B. Ellett	....	14.46	14.47	14.10	.....	[1]11.96	.....	.....
H. H. Hill	0.22	14.73	14.63	14.63	.....	12.22	.....	.....
M. I. Watkins	0.29	15.30	14.57	.....	[1]13.99	13.51	[1]11.25	13.38
M. L. Lowry	....	.....	.....	.....	.....	.....	12.76	.....
J. R. Tucker	0.32	[1]13.72	[1]13.96	14.88	14.35	13.31	13.87	13.33
A. K. Burke	0.28	14.62	14.60	14.70	14.47	12.90	13.00	13.03
H. D. Edmiston	0.35	14.83	14.21	14.39	.....	13.30	.....	12.96
Paul Rudnick, W. L. Latshaw	....	14.53	.....	14.31	14.85	13.24	13.27	13.34
L. B. Broughton	....	14.71	14.80	14.80	.....	13.58	.....	[1]14.28
S. C. Adams	....	14.39	14.47	14.51	.....	.....	.....	....
S. H. Wilson	0.28	14.46	14.42	14.02	14.10	12.74	12.74	13.06
Average	0.33	14.69	14.58	14.67	14.45	13.16	13.13	13.19

[1] Not included in average.

COMMENTS BY ANALYSTS.

W. C. Marti: Additional work done on methods for total phosphoric acid:

Two methods of solution were used: (1) Two grams of sample were dissolved in 20 cc. of hydrochloric acid and 10 cc. of nitric acid. (2) Two grams of sample were dissolved in 30 cc. of nitric acid. These solutions were diluted to 200 cc. and filtered and 20 cc. aliquots (equivalent to 0.2 gram of sample) were treated by the following methods:

(A) *Modified Sonnenschein method.*—Add molybdate solution and digest as usual. Wash precipitate three times by decantation through filter with solution containing 100 parts of molybdate solution, 20 parts of nitric acid (specific gravity 1.20) and 80 parts of water. Then wash with water and dissolve through filter into clean beaker. Precipitate with magnesia mixture and proceed in usual manner.

(B) *Modified Stöckman method.*—Evaporate solution in a porcelain dish adding 5 grams of ammonium nitrate toward the end, then transfer the dish to a sand bath. Evaporate to dryness and strongly heat over naked flame so that all nitrates and organic matter are destroyed. Digest residue with fuming hydrochloric acid until

ferric oxid is dissolved, then dilute, filter and evaporate filtrate with nitric acid until all the hydrochloric acid is expelled. Dilute with water and proceed as under official method.

(C) Regular official gravimetric method except washing yellow precipitate with ammonium nitrate solution.

(D) *Double precipitation method.*—After first precipitation with ammonium molybdate, wash by decantation. Dissolve in ammonium hydroxid and put into digestion bath, add nitric acid until almost neutralized and then add molybdate solution. From this point proceed as usual.

The results by the different methods agree very closely. All samples contained traces of iron.

Total phosphoric acid in Sample 1.

SOLUTION	METHOD (A)	METHOD (B)	METHOD (C)	METHOD (D)
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	18.43	18.49	18.39	18.35
2	18.46	18.59	18.46	18.49

P. L. Hibbard: Method 2 (A).—The Kjeldahl method gave a solution from which much silica separated on standing a few hours. Magnesia precipitates were much contaminated with both iron and silica.

Method 2 (B).—Magnesia precipitates from this solution very poor in quality due to much iron and silica. Presence of extra 5 cc. of nitric acid in phosphate solution improved them somewhat: Sample 1, 18.91 and 18.87; Sample 2, 17.33 and 17.44; and Sample 3, 15.21 and 15.21 per cent.

Double precipitation nearly removed the iron and completely removed the silica. This is less laborious than the dehydration method (2 (B) (a)) and far more effective in giving a pure magnesia precipitate. The operation is as follows: Decant off filtrate from the first yellow precipitate through a filter, retaining in the flask the yellow precipitate as much as possible. Dissolve the precipitate in ammonia, leaving solution slightly alkaline, add ammonium nitrate and water to make 100 cc. volume, warm to 65°, then add 20 cc. of molybdate solution, together with 5 cc. of nitric acid to reform the precipitate; digest as usual, and filter through same filter previously used. Proceed in ordinary way to form magnesia precipitate. Results were: Sample 1, 18.50 and 18.36; Sample 2, 17.09 and 17.25; Sample 3, 14.88 and 14.83 per cent.

Method 2 (B) (a).—The method for dehydration, given by the referee, is not effective and is of no use according to my experience. Dehydration in oven at 130°C. for 1 hour did not help much. Results were: Sample 1, 18.86 and 18.84; Sample 2, 17.76 and 17.70; Sample 3, 15.14 and 15.02 per cent. The main source of error with these solutions seems to be the iron, which is not removed by dehydration, but is mostly avoided by double precipitation.

Method 2 (B) (b).—Worked somewhat better than the aqua regia solution, probably due to citric acid present, but magnesia precipitate quite impure.

Method 3 (B) (b).—Same comment as for 2 (B) (b).

Method 2 (B) (c).—The citrate of ammonia magnesia mixture method seems to give good results and pure precipitates, but is objectionable on account of extra manipulation and the stirring machine required to carry it out properly.

L. S. Walker: By using the (a_6) method of making solutions, I found by the gravimetric method total phosphoric acid to be for Sample 1, 18.83 per cent; Sample

2, 17.15 per cent; Sample 3, 14.76 per cent. I also obtained the following results on the purification of the magnesium ammonium phosphate precipitate using (a_7) method of making solutions.

1. The magnesium ammonium phosphate precipitate was filtered through ashless filter paper, dried, burned off in a porcelain crucible, then dissolved in 1 to 1 hydrochloric acid, filtered, reprecipitated and weighed in the usual manner: Sample 1, 18.11 per cent; Sample 2, 16.89 per cent; Sample 3, 14.57 per cent.

2. The magnesium ammonium phosphate precipitate was filtered through ashless filter paper, dissolved in 1 to 1 hydrochloric acid, then evaporated to dryness on a steam bath to dehydrate, afterwards dissolved in a few drops of hydrochloric acid and a small quantity of water; filtered, precipitated, and weighed in the usual manner: Sample 1, 17.86 per cent; Sample 2, 16.40 per cent.

3. The magnesium ammonium phosphate precipitate was treated as in 2, but after being dehydrated in beaker, was transferred to porcelain beaker with hydrochloric acid and water, evaporated to dryness on a steam bath and finished on a hot plate; dissolved, filtered, reprecipitated, and weighed in the usual manner: Sample 1, 18.09 per cent; Sample 2, 16.30 per cent; Sample 3, 14.47 per cent. It seems evident that the silica in the magnesium ammonium phosphate precipitate had been rendered insoluble by this method; hence a trifle lower results were obtained.

By using (a_4) method of solution, results by the volumetric method were as follows: Sample 1, 18.75 per cent; Sample 2, 17.39 per cent; Sample 3, 15.01 per cent.

B. D. Wilson: Wagner flasks were not at hand and the citrate digestion was done in graduated flasks with round bodies instead of cylindrical, having the same size neck as the Wagner flasks.

J. C. Jurrjens: Much difficulty was experienced in getting rid of the silica in the case of Samples 2 and 3 with method (a_7) (hydrochloric and nitric acids) and the use of ammonia and ammonium nitrate was finally abandoned in the determination of phosphoric acid by this method in these two samples. All the magnesia precipitates were found to contain iron.

B. E. Curry: In the case of Samples 2 and 3 by the (a_7) method of making solution, the precipitate of magnesium pyrophosphate contained traces of iron. The same samples also showed the presence of iron by the dehydration method.

Benj. Freeman: I have followed the directions with the exception that under Total Phosphoric Acid 2 (B) (a) in dehydrating I evaporated to dryness three times instead of once. The determinations of iron and silica in the magnesia precipitates were accidentally spoiled. In the case of available phosphoric acid no iron and silica were found in the magnesia precipitates. I found that in making up the slag solutions by (a_4) that the addition of enough water to make the material move freely, prevented caking on addition of the sulphuric acid, and thus prevented also variation in results due to incomplete decomposition of the slag.

E. G. Proulx: In the estimation of total phosphoric acid, the three methods gave concordant results. The official gravimetric method using (a_4) method of making solution and the optional volumetric method were easier and shorter of manipulation. Traces of iron and silica were found in all magnesia precipitates after ignition in both total and available phosphoric acid determinations. The results on available phosphoric acid seem to check very well on Samples 1 and 2 but were not concordant on Sample 3, due to the difference in the solutions as they came from the rotary apparatus and not to the three methods of analysis which in all cases gave concordant results in the same solution. When available phosphoric acid in Sample 2 solutions (a), (b), and (c) was determined in the solutions after 48

hours standing, the molybdate method (a) gave 15.15 per cent, the volumetric method (b), 15.12 per cent, and the citrate ammonium magnesia method (c) gave 14.90 per cent. From the average result by each method it is apparent that the molybdate method gave results between the other two methods on all three samples and the optional volumetric method gave the highest results on all three samples. The analyst is of the opinion that the traces of iron and silica found in the magnesia precipitates after ignition were not present in sufficient amount to affect the results materially.

J. R. Tucker: Precipitates were tested after ignition for iron and silica. A trace of iron by the thiocyanate test was found in precipitates by methods 2 (A), 2 (B), and 2 (B) (a) for total phosphoric acid and by methods 3 (B) (a) and 3 (B) (b) for available phosphoric acid. No silicic acid was detected.

A. K. Burke: Tested all magnesia precipitates for iron and silica, but found only the merest traces of these substances present.

L. B. Broughton: The results obtained seem to indicate that it is necessary to remove the silica (SiO_2) from method (a_7) before making the determination. Method (a_4) seems to be preferable, as the results obtained by it compare favorably with those from (a_7) with the silica removed. For the determination of the available phosphoric acid the molybdate method is to be preferred. In the citrate of ammonia magnesia method the precipitates seemed to be contaminated with an impurity which makes it hard to filter and caused the results to be too high as compared with the molybdate method.

S. H. Wilson: Instructions were followed in every instance except in making the available phosphoric acid solution. Here, an ordinary 500 cc. measuring flask was used in place of the Wagner flask advised, and instead of using the rotary apparatus the samples were shaken by hand. In every case where solutions (a_4) and (a_7) were used, both silicia and iron were present in the magnesia precipitates.

DISCUSSION.

TOTAL PHOSPHORIC ACID.

The results obtained this year are encouraging but while they do not permit the drawing of conclusions they at least point out the direction in which the work must proceed in the future. After eliminating some results that are obviously too high or too low, the average results by the four methods show a close agreement on all three samples. The results of the individual analysts by the different methods and the results of the different analysts by the same methods, are, however, not as satisfactory, although the agreement is quite as good as has been obtained in the past by the methods that now are official for potash, nitrogen, fat, and crude fiber. It is possible that the lack of close agreement is due in part to unfamiliarity with the methods on the part of some of the collaborators but they have been in use in fertilizer laboratories for a number of years, and it seems improbable that the differences can be accounted for in this way. The differences are due almost entirely to the presence of iron and silica in the magnesia precipitate. By the (a_4) and (a_7) methods of solution, there may be both iron and silica in the magnesia precipitate

and in some cases the presence of calcium sulphate has been noted when the (a_4) method was used. By dehydrating the (a_7) solution, the soluble silica should be removed but the iron not necessarily; consequently the variations in the result by this method are undoubtedly due to the presence of iron in the final precipitate.

That some of the analysts found considerable quantities of iron and silica in the magnesia precipitate while others found only traces of these substances, demonstrates that more work must be done in order to determine the proper conditions that must be obtained to insure the elimination of both iron and silica at all times. In this connection it is interesting to note that in almost every instance where only traces of iron and silica were reported the results show a close agreement with the results by the volumetric method.

The results obtained by the modifications reported by Mr. Hibbard of California and those by the special methods reported by Mr. Marti of Michigan are no better than the results by the regular methods. The methods reported by the associate referee, Mr. Walker, for purifying the magnesium phosphate precipitate, offer a possible means of overcoming the difficulty. Further work along these lines is necessary.

The results of the individual analysts by the volumetric method show a much closer agreement than is true by the gravimetric methods. By this method the results are not influenced by the presence of iron or silica but the referee is of the opinion that it would be unwise for the association to take any action toward adopting it at this time.

AVAILABLE PHOSPHORIC ACID.

The results obtained for available phosphoric acid by the three methods do not show as close agreement as do the results for total phosphoric acid. The averages of the results by the three methods are fairly close but the results of the individual analysts show wide variations by all three methods. Although the molybdate method was provisionally adopted by the association in 1911 the results by it are no better than by the other methods.

The average by the volumetric method is slightly lower than by the other two but this fact has little significance since the variation in the results by the different analysts is great. From the results presented it is evident that the work on methods for determining available phosphoric acid in basic slag must be continued.

RECOMMENDATIONS.

It is recommended—

(1) That further work be done on methods for determining total phosphoric acid in basic slag.

(2) That further work be done on methods for determining available phosphoric acid in basic slag.

(3) That further attention be given to the presence of iron and silica in the magnesia precipitate and that methods designed to eliminate these substances be studied.

(4) That the methods outlined for total and available phosphoric acid be tried out with a synthetic solution representing as closely as possible a solution of the average basic slag.

A paper on "The use of sodium citrate for the determination of reverted phosphoric acid," by A. W. Bosworth, was read and published later in the *Journal of Industrial and Engineering Chemistry*, 1914, volume 6, number 3, page 227.

A. J. Patten announced by title a paper on "A simple method for preparing neutral ammonium citrate solution," by A. J. Patten and W. C. Marti, published in the *Journal of Industrial and Engineering Chemistry*, 1913, volume 5, number 7, pages 567–68.

Announcement was made by the Secretary, C. L. Alsberg, that the Secretary of Agriculture after careful consideration had decided that it was inadvisable for the Department of Agriculture to continue the publication of the proceedings of this association. The reasons given were that the association should not be subsidized by the Department and that the money which the Department has spent on the proceedings could be more profitably spent on publications of its own since a publication of this association would be very easily financed. The matter was referred to the executive committee for report.

REPORT ON NITROGEN.

By C. L. Hare, *Referee.*[1]

The work on nitrogen during the present year has been a continuation of that of 1912; namely, the investigation of the merits of the alkaline and neutral permanganate methods for determining the organic nitrogen activity in raw materials and mixed fertilizers, and trials of the proposed method for the estimation of nitrogen in nitrates.

The instructions sent to collaborators are practically identical with those sent out in 1912.

[1] Read by R. N. Brackett.

INSTRUCTIONS FOR COÖPERATIVE WORK.

In compliance with the recommendations for this year's work, there have been prepared the following samples for coöperative study:

Sample 1. Cottonseed meal.

Sample 2. Garbage tankage.

Sample 3. Mixture of Samples 1 and 2 with treated leather acid phosphate and muriate of potash.

Sample 4. c. p. Potassium nitrate.

METHODS.

The methods to be used are outlined below:

(1) Determine total nitrogen in Samples 1, 2, and 3 by one of the official methods.

(2) Determine available nitrogen in all samples by the alkaline and neutral permanganate methods.

Alkaline permanganate method.—Transfer an amount of material equivalent to 50 mg. of water-insoluble organic nitrogen (determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary) to a small mortar, add about 2 grams of powdered rock phosphate, mix thoroughly, transfer to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When much oil or fat is present, it is well to wash with ether before extracting with water.

Dry the residue at a temperature not exceeding 80°C. and transfer from the filter to a 500 to 600 cc. Kjeldahl distillation flask (round bottom preferred, but, if flat bottom is used, incline at an angle of 30°C.). Add 20 cc. of water, 15 to 20 small glass beads to prevent bumping, and 100 cc. of alkaline permanganate solution (25 grams of pure potassium permanganate and 150 grams of sodium hydroxid, separately dissolved in water, the solutions cooled, mixed, and made to volume of 1 liter). Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly, below distillation point, with very low flame, using coarse wire gauze and asbestos paper between flask and flame, for at least 30 minutes. Gradually raise the temperature and when danger (if any) from frothing has ceased, distill until 95 cc. of distillate is obtained, and titrate as usual. In case a tendency to froth is noted, lengthen the digestion period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. It is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation. The nitrogen thus obtained is the active water-insoluble organic nitrogen.

Neutral permanganate method.—Weigh a quantity of the fertilizer, equivalent to 50 mg. of water-insoluble organic nitrogen, on a moistened 11 cm. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add 1 gram of sodium carbonate, mix, and add 100 cc. o 2 per cent permanganate solution. Digest in a steam or hot-water bath for 30 minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of 10 minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate

amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.

(3) Determine nitrogen in Sample 4 as follows: To 0.5 gram of the nitrates in 600 to 700 cc. flask add 200 cc. of distilled water, 5 grams of powdered zinc, from 1 to 2 grams of ferrous sulphate, and 50 cc. of a 36° Baumé soda solution. In the neck of the flask place some glass wool and connect with the distilling apparatus. Distill off the ammonia and collect as usual in decinormal sulphuric acid and titrate.

It is requested that results be reported on the percentage basis as follows: Total nitrogen, water-soluble organic nitrogen, active water-insoluble nitrogen, inactive water-insoluble nitrogen.

RESULTS OF COLLABORATION.

Sample 1. Cottonseed meal.

ANALYST	TOTAL NITROGEN	WATER INSOLUBLE NITROGEN	WATER SOLUBLE NITROGEN	ACTIVE WATER INSOLUBLE NITROGEN		ACTIVITY	
				Alkaline permanganate method	Neutral permanganate method	Alkaline permanganate method	Neutral permanganate method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
G. F. Lipscomb, Clemson College, S. C.	6.32	5.39	0.93	2.59	5.02	48.20	93.30
F. N. Smalley, Savannah, Ga.	6.45	6.09	0.36	2.80	5.56	46.00	91.30
J. B. Jackson, Auburn, Ala.	6.40	5.80	0.60	2.80	5.21	48.20	90.00
S. Adler, Auburn, Ala.	6.40	5.94	0.46	3.63	5.60	61.10	94.00
C. L. Hare, Auburn, Ala.	6.27	5.70	0.57	3.13	5.22	55.00	91.60
J. C. Jurrjens, Madison, Wis.	[1]6.37	....	....	....	....	.....	.....
O. F. Jensen, East Lansing, Mich.	[1]6.50	6.04	0.46	3.58	5.48	59.00	90.80
E. F. Bailey, New Haven, Conn	6.47	5.97	0.50	3.63	5.72	60.80	95.80
G. L. Davis, New Haven, Conn.	6.49	5.99	0.50	3.56	5.79	59.50	96.60
"A", Burlington, Vt.	6.45	6.01	0.44	3.52	5.71	58.55	95.00
"B", Burlington, Vt.	6.45	5.99	0.46	3.47	5.65	58.00	94.30
L. S. Walker, Amherst, Mass.	6.46	5.96	0.50	3.40	5.70	57.00	95.60
A. T. Charron, Ottawa, Conn.	6.08	5.36	0.72	2.10	5.87	34.50	93.25
T. D. Jarrell, College Park, Md.	6.41	5.97	0.44	2.12	....	.....	.....
Average	6.39	5.86	0.53	3.10	5.54	53.82	93.46

[1] Modified Gunning method.

Sample 2. Garbage tankage.

ANALYST	TOTAL NITROGEN	WATER INSOLUBLE NITROGEN	WATER SOLUBLE NITROGEN	ACTIVE WATER INSOLUBLE NITROGEN		ACTIVITY	
				Alkaline permanganate method	Neutral permanganate method	Alkaline permanganate method	Neutral permanganate method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
G. F. Lipcomb	3.28	2.74	0.54	0.58	1.36	21.28	49.62
F. N. Smalley	3.04	2.82	0.22	0.69	1.80	24.50	63.80
J. B. Jackson	3.09	2.84	0.25	0.70	1.57	24.65	55.30
S. Adler	2.98	2.85	0.13	1.00	1.91	35.00	67.00
C. L. Hare	3.09	2.84	0.25	0.83	1.76	29.20	62.00
J. C. Jurrjens	[1]3.01	....	....	....	....	.....	.....
O. F. Jensen	[1]2.94	2.78	0.16	0.84	1.66	30.20	60.00
E. F. Bailey	3.00	2.77	0.23	0.78	1.80	28.20	65.00
G. L. Davis	2.93	2.73	0.20	0.77	1.96	24.50	71.80
"A"	3.05	2.89	0.16	0.88	1.97	30.40	68.20
"B"	2.95	2.86	0.09	0.83	1.90	29.00	66.40
L. S. Walker	2.98	2.78	0.20	0.78	1.85	28.10	66.60
A. T. Charron	3.01	2.65	0.36	0.83	1.95	31.30	73.60
T. D. Jarrell	3.01	2.50	0.51	0.57	....	.....	.....
Average	3.03	2.77	0.25	0.78	1.79	28.03	64.11

[1] Modified Gunning method.

Sample 3. Mixture of cottonseed meal and garbage tankage with treated leather and acid phosphate with muriate of potash.

ANALYST	TOTAL NITROGEN	WATER INSOLUBLE NITROGEN	WATER SOLUBLE NITROGEN	ACTIVE WATER INSOLUBLE NITROGEN		ACTIVITY	
				Alkaline permanganate method	Neutral permanganate method	Alkaline permanganate method	Neutral permanganate method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
G. F. Lipscomb	2.60	2.06	0.54	0.63	1.53	30.68	74.65
F. N. Smalley	[1]2.38						
	2.29	2.13	0.16	0.76	1.75	35.70	82.10
J. B. Jackson	2.38	2.08	0.30	0.79	1.71	38.00	82.20
S. Adler	2.21	2.06	0.15	1.00	1.69	48.55	82.00
C. L. Hare	2.38	2.08	0.30	0.85	1.68	40.90	80.80
J. C. Jurrjens	[1]2.23	....	....	....	....	.....	.....
O. F. Jensen	[1]2.23	2.05	0.18	0.92	1.40	45.00	68.30
E. F. Bailey	[1]2.24	2.10	0.14	....	....	.....	.....
G. L. Davis	[1]2.21	2.06	0.15	0.93	1.66	45.10	80.50
"A"	2.32	2.05	0.27	0.93	1.70	45.40	83.00
"B"	2.21	2.00	0.21	0.87	1.66	43.50	83.00
L. S. Walker	2.23	2.04	0.19	0.84	1.60	41.20	78.40
A. T. Charron	2.15	1.98	0.17	0.81	1.50	41.00	75.75
T. D. Jarrell	2.22	1.92	0.31	0.87	....	.....	.....
Average	2.28	2.05	0.23	0.85	1.62	41.37	79.15

[1] Modified Gunning method.

Sample 4. c. p. Potassium nitrate.

ANALYST	NITROGEN	
	Official method	Proposed method
B. F. Robertson	13.75	13.68
F. N. Smalley	.....	13.72
J. B. Jackson	.....	13.82
S. Adler	13.74	13.84
C. L. Hare	13.85	13.79
O. F. Jensen	.....	13.80
E. M. Bailey	.....	13.79
T. D. Jarrell	13.50	13.50
Average	13.71	13.74

COMMENTS OF ANALYSTS.

A. T. Charron: Organic nitrogen activity.—The instructions for the alkaline permanganate method directed to dry the residue at a temperature not exceeding 80°C. and to transfer from the filter to a 500 to 600 cc. flask. In practice it was found impossible to detach completely the material from the filter. The loss occasioned by some of the residue adhering persistently to the filter must have impaired materially the accuracy of the results obtained. When the residue was transferred with the filter to the distillation flask the results obtained were so erratic that they are not here reported. This was undoubtedly due to the fact that the organic matter of the filter decomposed a certain portion of the alkaline permanganate, thus lessening its effect upon the nitrogenous organic matter of the fertilizer. Frothing during distillation even after prolonged digestion caused considerable trouble. The fact that the duplicate results obtained were fairly concordant gives no assurance of their accuracy because the same conditions obtained as to quantity both of sample taken and of reagents used. The neutral permanganate method gave generally more closely concordant results than the alkaline permanganate method.

Nitric nitrogen.—The method proposed for the determination of the nitrogen in nitrates gave very satisfactory duplicate results. It was found necessary, however, to add a small piece of paraffin wax to the distilling mixture to prevent troublesome frothing.

B. F. Robertson: Several results obtained by the ferrous-sulphate-zinc-soda method were rejected as they were obviously too low. The analyst thinks that this method is rapid, and will in the hands of a skillful and experienced worker give accurate results.

T. D. Jarrell: All total nitrogen determinations were made by the official Gunning modification of the Kjeldahl method. The averages show exactly the same results on the c. p. potassium nitrate by both the zinc-iron method and the official Gunning method. The zinc-iron method has the advantage of being much shorter. The official Gunning method was modified to the extent of allowing the nitrate to stand overnight in the salicylic acid mixture instead of only 10 minutes. It has been my experience to find that the highest results are obtained by allowing the nitrate to stand at least several hours in salicylic acid mixture before digestion. I was unable to obtain satisfactory results by the neutral permanganate method due, I believe, to the fact that all the potassium permanganate was reduced during the digestion in the water bath.

DISCUSSION.

It will be noted that with one or two exceptions the results on organic nitrogen activity in the three samples are fairly uniform; in fact, the results agree more closely than might be expected in methods which do not lay claim to great accuracy. The results of chemists who have had little experience with the methods agree well with those of Eastern chemists who have been using the methods for a number of years. It may be said, however, that some laboratories report that sometimes duplicate determinations do not show satisfactory agreement and additional determinations are necessary before acceptable results can be secured. The results by the ferrous-sulphate-zinc-soda method for nitrogen in nitrates are satisfactory though few in number.

RECOMMENDATIONS.

It is believed that results obtained this year, together with those of 1912, indicate that analysts working with either of the two methods for organic nitrogen activity can secure results agreeing fairly well with results obtained in other laboratories where the same method is employed. Although the referee believes that the methods form a fair basis for arriving at the relative activity of the organic nitrogen in various fertilizing materials and that either method will serve to differentiate the good from the bad, the relatively small number of results received—about 20 for the two years—is scarcely sufficient to warrant a positive recommendation that the association adopt the methods.

It is recommended that the ferrous-sulphate-zinc-soda method be provisionally adopted.

W. D. Bigelow extended an invitation to the members and visitors at the meeting to attend a smoker at the laboratories of the National Canners Association that evening at 8 o'clock.

REPORT ON DETERMINATION OF POTASH.

By H. B. McDonnell, *Referee.*

This year the referee was given no instructions as to the line of work to be pursued. Further tests were made of the gravimetric cobaltinitrite and perchlorate methods as used last year and with some minor variations (the laboratory work was done by T. D. Jarrell). The results obtained were unsatisfactory and it was not deemed expedient to ask the association to test the methods further until decided improvements are made.

The perchlorate method seemed promising but the solubility of the precipitate in strong alcohol and the difficult solubility of the impurities, including barium chlorid, in the alcohol cause unreliable results.

As stated in the report of last year, satisfactory results have been obtained by using denatured alcohol, instead of straight alcohol, for washing the potassium platinic chlorid. It was deemed of sufficient importance for further test (see Instructions).

In the official method for potash, as adopted in 1912, there is doubt as to the necessity of boiling the water solution with hydrochloric acid and, as this consumes time and prevents the determination of chlorin in the same solution, it seemed desirable that this point should be tested. As work on these points with one or two samples would not be of much value, those analysts willing to coöperate were asked to use their own samples. The following letter was sent out to 17 chemists who had signified their willingness to coöperate.

INSTRUCTIONS.

Dear Sir: The referee on potash has, with the assistance of T. D. Jarrell, tested further both the gravimetric cobalti-nitrite and perchlorate methods, using some variations, but is convinced that these methods are so much inferior to the platinum method that he can not recommend further work by the association at this time.

Two other points, however, are recommended for coöperative work:

(1) In the potash method recently adopted there is doubt as to the necessity for the addition of 2 cc. of hydrochloric acid to the water solution and heating the same to boiling. You are requested to test this on some of your own samples, using the official method and the same method omitting the "2 cc. of hydrochloric acid and boiling." If this is unnecessary it should be omitted, as it consumes time and interferes with the determination of chlorin, necessitating another solution for the latter.

(2) As stated last year, denatured alcohol gives good results when used in the determination of potash. You are requested to try this also. Commercial denatured alcohol is generally made from about 100 parts of 90 per cent alcohol, 10 parts of methyl alcohol and 0.5 parts of gasoline. This becomes somewhat cloudy on adding water, due, probably, to the partial separation of the gasoline, but this appears to make no difference when used as wash for the potassium-platinic chlorid precipitate.

RESULTS.

No report has been received in regard to the use of hydrochloric acid except from our own laboratory. Mr. Jarrell, working on 75 samples, made duplicate tests from the same flasks, one by the official method, the other modified by omitting the boiling of the solution with 2 cc. of hydrochloric acid, reports an average by the official method, 4.22 per cent, and by the modification, 4.13 per cent of potassium oxid, showing an average of 0.09 per cent higher by the official. This difference may be

only accidental, as higher results were obtained by the modification in about one-half of the tests.

Mr. Jarrell reports, as stated above, that denatured alcohol gives results comparable with ethyl alcohol when used in same strength.

RECOMMENDATIONS.

It is recommended that further coöperation be secured in testing:

(1) The use of denatured alcohol for washing potassium platinic chlorid.

(2) The necessity, or otherwise, for the use of hydrochloric acid in the water extract in potash determinations.

REPORT ON AVAILABILITY OF POTASH.

By E. E. Vanatta, *Associate Referee.*[1]

The Agronomy Department of the University of Missouri has undertaken in coöperation with the associate referee to determine the effect of different forms of potash upon growing plants. The work for the present year has been of a preliminary nature on barley grown in pots, with results as reported in the following paper. It was determined to study also the effect of manure in rendering the insoluble potash of soils available as plant food as measured by the solubility in water. In this study a sample of Missouri soil containing 1.52 per cent of potash as determined by the J. L. Smith method was used. Six samples were prepared as follows:

Sample 1. 150 grams of untreated air-dry soil.

Sample 2. 150 grams of air-dry soil kept moist for 60 days.

Sample 3. 30 grams of air-dried cow dung.

Sample 4. 30 grams of air-dried cow dung kept moist for 60 days.

Sample 5. 150 grams of air-dry soil intimately mixed with 30 grams of air-dried cow dung kept in this air-dry condition for 60 days.

Sample 6. 150 grams of air-dry soil intimately mixed with 30 grams of air-dried cow dung and kept moist for 60 days.

At the end of the 60 days each of these samples was transferred to a large filter paper and washed thoroughly with about one and one-half liters of hot water. The filtrates were evaporated to dryness and ignited with the addition of sulphuric acid. In the residue the potash was determined by the official method with results as follows:

[1] Read by P. F. Trowbridge.

Determination of potash by official method.

Sample	Grams of soluble potash
1 (dry soil)	0.0042
	0.0028
Average	0.0035
2 (moist soil)	0.0035
	0.0035
Average	0.0035
3 (dry manure)	0.0915
	0.0862
Average	0.0888
4 (moist manure)	0.0931
	0.0748
Average	0.0840
5 (dry soil-manure mixture)	0.0573
	0.0597
Average	0.0585
6 (moist soil-manure mixture)	0.0295
	0.0214
Average	0.0255

The residue from the washing in each case was boiled with about 500 cc. of water for about 2 hours; the solution was decanted and the residue was again boiled with 500 cc. of water for about 2 hours; the solution was decanted, the residue transferred to a filter and thoroughly washed with hot water. The combined filtrates for each sample were evaporated to dryness and ignited with sulphuric acid. In the residue the potash was determined by the official method with the following results:

Potash in second washing of samples.

Sample	Grams of soluble potash
1 (dry soil)	0.0104
	0.0092
Average	0.0098
2 (moist soil)	0.0166
	0.0131
Average	0.0148
3 (dry manure)	0.0058
	0.0028
Average	0.0043
4 (moist manure)	0.0066
	0.0065
Average	0.0066

Potash in second washing of samples—Continued.

Sample	Grams of soluble potash
5 (dry soil-manure mixture)	0.0103
	0.0133
Average	0.0118
6 (moist soil-manure mixture)	0.0160
	0.0175
Average	0.0168

The results show that the second washing removed fully twice as much potash from the soil as was removed by the first treatment. The first treatment removed nearly all of the potash from the manures, the moistened manure yielding slightly less potash than the dry manure. The soil and manure mixtures gave much less potash than did the manure alone, and the dry mixture gave more than twice as much potash as the moistened mixture. The second treatment yielded considerably more potash from both the dry and moistened mixtures than from the manures alone, but not as much as that obtained from the sum of the soil and manure under the similar conditions. The sum of the two determinations as shown in the following table indicates that the manure in combination with the soil decreases the amount of water-soluble potash and the moistened mixture seems to retain much more of the potash than does the dry mixture.

Average of combined weight of potash in both washings.

Sample	Grams of soluble potash
1 (dry soil)	0.0133
2 (moist soil)	0.0183
3 (dry manure)	0.0932
4 (moist manure)	0.0905
5 (dry soil-manure mixture)	0.0703
6 (moist soil-manure mixture)	0.0423

It is recommended by the associate referee that this study be continued another year and that the effect of decomposing green material be studied.

THE DETERMINATION OF THE AVAILABILITY OF POTASH IN FELDSPATHIC FERTILIZER BY MEANS OF POT EXPERIMENTS.

By M. F. Miller and E. E. Vanatta.

The experiment here reported was planned to throw light on the availability of potash in feldspathic fertilizer. It was carried out partly in the small greenhouse belonging to the Entomology Department of the University of Missouri and partly out of doors. Three-gallon stone jars were used. The soil experimented upon consisted of 4 gallons of river sand to

one-half gallon of silt loam, the latter being added simply to give some body to the sand but in too small a quantity to supply any great amount of potash to the growing plants. Barley was the plant used as an indicator.

TRIAL I.

Six pots were run in duplicate with the following treatments:

Pot 1: Sodium nitrate, dried blood, and acid phosphate, plus potassium chlorid.

Pot 2: Sodium nitrate, dried blood, and acid phosphate, plus potassium sulphate.

Pot 3: Sodium nitrate, dried blood, and acid phosphate, plus the minimum dose of feldsphatic fertilizer.

Pot 4: Sodium nitrate, dried blood, and acid phosphate, plus double the minimum dose of feldspathic fertilizer.

Pot 5: Sodium nitratė, dried blood, and acid phosphate, plus four times the minimum dose of feldspathic fertilizer.

Pot 6: Sodium nitrate, dried blood, and acid phosphate, plus six times the minimum application of feldspathic fertilizer.

Both potassium chlorid and potassium sulphate were applied at the rate of 800 pounds per acre in the pots. The feldspar was applied in the minimum quantity, so that the soluble potash figured at 3.49 per cent would be equivalent to 50 per cent soluble potash in the application of potassium sulphate. This made the minimum application at the rate of 11,450 pounds per acre, the next 22,900, the next 45,800, and the maximum 68,700 pounds. The reason for making such heavy applications is that in ordinary pot work the application of fertilizer per acre is usually doubled or tripled or quadrupled because of the small amount of feeding space for the roots.

It was found that these applications of the feldspathic fertilizer were too heavy as germination was greatly interfered with in the heavier treatments. The pots were replanted a number of times, but as germination was always poor it was concluded that the applications were heavy enough to be caustic and the whole experiment was repeated.

TRIAL II.

In the second trial the applications were made at the following rates per pot:

POT NO.	SODIUM NITRATE	DRIED BLOOD	ACID PHOSPHATE	POTASSIUM CHLORID	POTASSIUM SULPHATE	FELDSPAR
1.....	1.24	2.48	6.20	2.48	....	....
2.....	1.24	2.48	6.20	....	2.48	....
3.....	1.24	2.48	6.20	....	....	35.5
4.....	1.24	2.48	6.20	....	....	71.0
5.....	1.24	2.48	6.20	....	....	106.0
6.....	1.24	2.48	6.20	....	....	142.0

The minimum application of feldspar here carries the same amount of soluble potash as is applied in potassium sulphate on Pot 2, figuring the amount of potash in the feldspathic fertilizer as 3.49 per cent and that in the potassium sulphate at 50 per cent. The second application of the feldspathic fertilizer would seem to be double this, the third triple and the fourth quadruple. The following table shows the rate per acre of the above applications:

POT NO.	SODIUM NITRATE	DRIED BLOOD	ACID PHOSPHATE	POTASSIUM CHLORID	POTASSIUM SULPHATE	FELDSPAR
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
1.....	200	400	1000	400	...	...
2.....	200	400	1000	...	400	...
3.....	200	400	1000	...	...	5725
4.....	200	400	1000	...	...	11450
5.....	200	400	1000	...	...	17175
6.....	200	400	1000	...	....	22900

The pots were watered with distilled water from time to time to maintain the proper moisture content and after they were well started they were removed to the open air where the rainfall was allowed to supply part of the moisture needed. They were allowed to grow to full maturity with the results given below in weight of grain and straw. It was noticed that the pots giving the largest total dry weight were the last to mature, otherwise there was little difference observed in the appearance of the plants.

SPECIAL ADDITIONS	STRAW DRY WEIGHT	GRAIN DRY WEIGHT	TOTAL CROP WEIGHT	AVERAGE RELATIVE WEIGHT OF CROP
	grams	*grams*	*grams*	*grams*
Nitrogen, phosphorus, potassium chlorid	10.2538 11.1837	0.9462 1.0163	11.2 12.2	11.7
Nitrogen, phosphorus, potassium sulphate	13.1113 13.9187	3.2887 2.1813	16.4 15.1	15.7
Feldspar A..................... Feldspar B.....................	6.2666 11.1000	1.5334 1.7000	8.8 12.8	10.8
Feldspar B..................... Feldspar A.....................	11.0557 9.8036	0.7443 1.1964	12.8 11.0	11.9
Feldspar B..................... Feldspar B.....................	8.7830 9.9400	1.0170 1.6600	9.8 10.6	10.2
Feldspar A..................... Feldspar B.....................	10.5838 11.9827	1.8162 1.8173	11.4 13.8	12.6

In the repetition of this experiment the amounts of the feldspathic fertilizer, as well as the potassium chlorid and potassium sulphate applications will be still further reduced.

THE PERCHLORATE AND GRAVIMETRIC COBALTI-NITRITE METHODS FOR THE DETERMINATION OF POTASH.

By T. D. Jarrell.

PERCHLORATE METHOD.

The principle of the perchlorate method is based on the fact that potassium perchlorate is insoluble in strong alcohol containing a trace of perchloric acid. The low results which the writer has found by this method in comparison with the platinic chlorid method are due, in his opinion, to the fact that potassium perchlorate is slightly soluble in the alcohol wash. Chemically pure potassium chlorid was taken as a basis to prove this fact because it is free from all foreign salts and because the potassium perchlorate would not contain any barium chlorid. A precipitate of potassium perchlorate weighing 0.6492 gram obtained from the c.p. salt was washed with 50 cc. of alcohol wash (95 per cent alcohol containing 1 cc. of perchloric acid per 200 cc. of alcohol) and finally with 10 cc. of absolute alcohol, allowing 5 minutes for the washing, and the weight was reduced 0.0086 gram or 1.4 per cent. The washing was repeated under the same conditions and the weight was again reduced at about the same ratio. Therefore, the writer believes that potassium perchlorate is slightly soluble in the alcohol wash as outlined in the method.

As the perchloric method cannot be applied in the presence of sulphates, they must be removed by the addition of sufficient barium chlorid to precipitate them. It is nearly impossible to precipitate all the sulphates as barium sulphate without getting an excess of barium chlorid and many times unless extreme care and patience are used, a large excess of barium chlorid. In that case some of the barium chlorid will not be washed out and will be weighed as potassium perchlorate. Barium chlorid is only slightly soluble in 95 per cent alcohol; 0.6528 gram of barium chlorid was weighed in a prepared Gooch crucible and washed with 50 cc. of alcohol "wash" as previously described and finally with 10 cc. of 95 per cent alcohol, allowing 5 minutes for the washing, reducing the original weight but 0.1482 gram, showing a residue of 0.5046 gram of barium chlorid. It is thus shown conclusively that alcohol is a very poor solvent for barium chlorid.

The following table gives a comparison of the perchlorate method with the platinum method on a sample of c.p. potassium chlorid and several mixed fertilizers.

It is seen that the perchloric method here gives results lower in every case than the platinum method. An effort was made to use but the slightest excess of barium chlorid. The only accountable reason for the low results is that some of the potassium perchlorate is dissolved by washing.

Comparison of results by the perchlorate and platinum methods.

SAMPLE	POTASH	
	Perchlorate method	Platinum method
	per cent	*per cent*
c. p. potassium chlorid....	61.68 61.56	63.04 62.64
Average.................	61.62	62.84
25330.....................	5.37 5.66 5.85	5.78 5.78
Average.................	5.63	5.78
25496.....................	10.21 10.00 10.44	10.76 10.92
Average.................	10.22	10.84
25306.....................	2.30 1.92 1.74 1.91 1.80	2.92 2.96 3.08
Average.................	1.93	2.99

Even should the perchlorate method give results which agree very closely with the platinum method, the writer is unable to see any advantage it has over the latter method. It requires much more time to carry on a series of determinations. All of the sulphates must be removed causing an extra filtration besides the time it takes to add the barium chlorid carefully.

If it were possible to find a "wash" that potassium perchlorate is not in the least soluble in and one that would completely dissolve barium chlorid and other foreign salts in the precipitate at the same time, it is believed that results could be obtained which would compare favorably with those obtained by the platinum method.

GRAVIMETRIC COBALTI-NITRITE METHOD.

The cobalti-nitrite method for the determination of potash in fertilizers has been investigated by the association for several years with only partial success, yet the method and results have proved encouraging and final success seems probable.

The principle of the cobalti-nitrite method is based on the fact that a mixture of sodium nitrite and cobalt acetate and acetic acid made up to a specified strength, precipitates a potassium salt as di-potassium-sodium-cobalti nitrite ($K_2NaCo(NO_2)_6$). The cobalti-nitrite reagent is very

unstable; it not only decomposes on several days standing but it decomposes during evaporation with the potassium salt.

The volume of the potash solution, the volume of the reagent, the time of evaporation, and many other conditions have been found to have a tendency to produce differences in the results. The reagent when heated nearly to boiling in solution with a potash salt is partly decomposed, leaving a pink solution. This was especially true when the reagent was added to a large volume of potash salt, taking at least an hour for the evaporation.

Most of the work noted in this paper was conducted upon c.p. potassium chlorid, since a method which does not work well on c.p. salts cannot be depended upon with substances of a complex nature. Some determinations were also made on mixed fertilizers showing a comparison of results with the cobalti-nitrite method and the platinum method.

On c.p. potassium chlorid results ranging from about 55 per cent to 61 per cent of potash were found when the reagent was added to 50 cc. solution; the higher results (61 per cent), however, were found by adding 25 cc. of the reagent while lower results (55 per cent) were secured by adding 15 cc. of reagent.

The table on page 32 shows a comparison of results obtained by the cobalti-nitrite and platinum methods on a sample of c.p. potassium chlorid and several mixed fertilizers.

The results by the cobalti-nitrite method were obtained by adding 25 cc. of the reagent to 10 cc. of the potash solution and evaporating to a thick sirup. The results seem to agree in most cases fairly well with those by the platinum method.

The directions sent out by the referee on potash in 1912 direct the collaborators to add about 10 cc. of the reagent to about 30 cc. of the potash solution and then to evaporate to a thick sirup. This method was tried thoroughly on several mixed fertilizers without success. The results were discordant, the difference sometimes being over 1 per cent on aliquots taken from the same solution. The writer believes this is due to the fact that the reagent is decomposed by continual heating, and this decomposition is hastened by dilution. It is necessary to have an excess of undecomposed reagent present at the conclusion of the evaporation in order to secure concordant results.

At the conclusion a series of determinations were made on the same c.p. potassium chlorid as used at first, following as closely as possible the same conditions as followed at first, in order to learn whether after more experience with the method, results could be obtained which would agree favorably with results obtained as indicated in the table. The results found were: 61.16, 60.01, 61.71, and 61.47 per cent of potash. The average of the results obtained the first time on the c.p. potassium chlorid was 63.13 per cent of potash, agreeing very closely with the theory, while the results obtained after increased skill and familiarity with the

Comparison of results by the cobalti-nitrite and platinum methods.
(Theory: Potassium chlorid = 63.17 per cent of potash.)

SAMPLE	POTASH			REMARKS
	Cobalti-nitrite method	Cobalti-nitrite method (Itano's modification)	Platinum method	
	per cent	*per cent*	*per cent*	
c. p. potassium chlorid:	63.23 63.29 62.87	....	63.04 62.64	Aliquots taken from same flask.
Average..................	63.13	....	62.84	
25330..........................	6.06 6.16 6.20 6.23	....	5.78 5.78	Aliquots taken from same flask.
Average..................	6.16	....	5.78	
25496..........................	10.49 10.39 10.42	10.84 10.64 10.46 10.69	10.76 10.92	Aliquots taken from same flask.
Average..................	10.43	10.66	10.84	
25306..........................	2.99 2.97 3.06 [1]2.86	2.99 3.05 3.03 3.03	2.92 2.96 3.08	Aliquots taken from same flask.
Average..................	3.01	3.03	2.99	

[1] Not included in average; added reagent to 50 cc. of potash solution.

method showed an average of only 61.11 per cent of potash—a difference of 2.02 per cent. It is, however, very difficult, if not impossible, to duplicate exactly the necessary conditions from time to time, and as the slightest variations in handling the method produce wild results, the method in its present form is, in the writer's opinion, unreliable. If the time of evaporation could be accurately controlled, and if the proper dilution of each sample could be always known, it seems probable that accurate results could be obtained.

A large number of results are not tabulated because they were so erratic; for instance, a great many determinations were run on both c.p. potassium chlorid and mixed fertilizers, adding the reagent to from 25 to 50 cc. of the potash salt before evaporating, getting results which many times varied several per cent in the same set and sometimes from the same aliquot.

It is the writer's opinion that the gravimetric cobalti-nitrite method for the determination of potash in fertilizers must be greatly improved before it can be successfully used.

REPORT ON SOILS.

By G. S. Fraps, *Referee.*

The work of the referee on soils may be discussed under two headings:

(1) Coöperative work on the Veitch method for acidity.

(2) Laboratory work on methods for humus.

COÖPERATIVE WORK ON ACIDITY.

The following instructions were sent out to those analysts planning to coöperate.

INSTRUCTIONS FOR WORK ON SOILS.

The coöperative work on soils will be confined to the study of the Veitch method for acidity. Three acid samples will be sent. It is requested that the acidity be determined by the method here described; the method of testing for acidity is given for the information of the collaborators.

TEST FOR ACIDITY IN SOILS.

Test of water.—Place 100 cc. of distilled water in a Jena beaker and boil with a few drops of phenolphthalein as directed in test. If the water is alkaline, so report; if the water is not alkaline, secure a quantity of it, and use it for the test described. If new water has been made, make a new test. Always test the water actually used, and do not use any which is alkaline.

Treat 10 grams of soil with 100 cc. of water in a Jena flask, allow to stand overnight, draw off 50 cc. of the supernatant liquid and boil with a few drops of phenolphthalein in a covered Jena beaker until the appearance of a pink color, or to a volume of 5 cc. The pink color indicates alkalinity. Report merely whether acid or alkaline.

If acid, report "Acid—"
If alkaline, report "Pink+"

DETERMINATION OF ACIDITY.

Lime water.—Place 10 grams of quicklime in 2,000 cc. of water and allow to stand at least 24 hours, shaking every hour; filter and protect from the air in glass-stoppered bottles. Titrate 50 cc. with fifth-normal acid and 1 cc. of phenolphthalein, until color just disappears; calculate the quantity of lime per cubic centimeter. One cubic centimeter of fifth-normal acid is equivalent to 0.0056 gram of calcium oxid. The strength of the lime water must be determined from time to time, as it is likely to take up carbon dioxid from the air and become weaker.

Determination.—Weigh out 5 grams of soil and place in a small evaporating dish; add the required amount of standard lime water, then 50 cc. of tested water, and evaporate the solution to dryness on the water bath. Wash it into an Erlenmeyer flask with 100 cc. of tested water and allow to stand 24 hours. Pipette off 50 cc., taking care not to disturb the soil. Filter if necessary in order to get a clear solution. Add 1 cc. of phenolphthalein and boil the solution until a pink color appears or to 5 cc. if no color appears. The results are calculated as parts per million of lime required to neutralize the soil. Jena glassware must be used, as ordinary glassware may give an alkaline reaction when boiled with water.

In estimating the acidity of a number of soils, it is best to test first for acidity or alkalinity on all samples at once. Treat such soils as are acid with 1 cc. of lime

water as directed, those acid to 1 cc. with 2 cc., and so on with 5, 10, 20 and 50 cc. Then make other tests to narrow the limits of the method until the reaction is acid with a volume of lime water which differs by 1 cc. from a volume with which it is alkaline; for example, the reaction is acid with 12 cc. and alkaline with 13 cc. When the acidity requires over 20 cc. of lime water, the difference between the acid and alkaline condition may be allowed to be 2 cc. of lime water. This method is much quicker than running a number of tests with different amounts of lime water at the same time upon the same soil. On the samples sent out, however, it will probably be better to run with 4, 10, and 15 cc. of lime water the first time.

Please report (a) the quantity of lime water at which the soil is alkaline and acid; (b) limits within which the soil is alkaline or acid, in parts per million of lime.

REPORTS OF ANALYSTS.

Reports of the analysts are given in the following tables:

TABLE 1.

Parts per million of lime (CaO) with which soils were acid or alkaline.

ANALYST	SOIL 1		SOIL 2		SOIL 3	
	Acid	Alkaline	Acid	Alkaline	Acid	Alkaline
J. A. Bizzell, New York..	717	956	1434	1673	0	239
E. Van Alstine, Illinois (August).............	914	1139	1600	1823	0	0
E. Van Alstine, Illinois (June)...............	684	912	1126	1366	0	0
H. C. McLean, New Jersey...............	1008	1260	1764	2016	0	252
J. E. Harris, Michigan...	1377	1607	2066	2296	0	229
R. C. Thompson, Arkansas.............	980	1078	1078	1176	0	98
C. B. Lipman, California	1110	1320	1110	1540	0	220
O. C. Smith, Missouri....	880	1100	1320	1760	0	220
Chemists, Texas.........	1248	1442	1442	1664	0	208
Average (9)...........	991	1202	1438	1702	0	209

TABLE 2.

Volume of lime water with which soils were acid or alkaline.

ANALYST	SOIL 1		SOIL 2		SOIL 3	
	Acid	Alkaline	Acid	Alkaline	Acid	Alkaline
	cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
J. A. Bizzell............	3	4	6	7	0	1
E. Van Alstine (August)	4	5	7	8	..	0
E. Van Alstine (June)...	3	4	5	6	..	0
H. C. McLean..........	4	5	7	8	0	1
J. E. Harris.............	6	7	9	10	0	1
R. C. Thompson.	5	5.5	5.5	6	0	0.5
C. B. Lipman...........	5	6	5	7	0	1
Chemist, Texas.........	6	7	7	8	0	1
O. C. Smith.............	4	5	6	8	0	1
Average.............	4.4	5.4	6.4	7.6	0	0.9

E. Van Alstine: The samples were pulverized in an agate mortar and passed through a 100 mesh sieve. Two series of tests were made (in June and in August) with different results (see Table 1).

H. C. McLean: With the original Veitch method, using 12.6 gram portions of soil, the following results were secured:

SOIL	VOLUME LIME WATER		PARTS PER MILLION OF LIME	
	Acid	Alkaline	Acid	Alkaline
	cc.	*cc.*		
1......	7.5	8.0	750	800
2......	13.0	13.5	1300	1350
3......	0.5	0.75	50	75

These results are much lower than those with the modified method.

DISCUSSION.

There is somewhat more variation in the results secured by the lime-water method than is desirable. It is possible that further study may show the cause of these variations, and allow us to secure more closely agreeing results. The method is useful, however, in distinguishing soils which are acid, and showing, in a general way, their requirements for lime.

METHODS FOR DETERMINATION OF HUMUS.

SMITH METHOD.

O. C. Smith of the Missouri Agricultural Experiment Station, (*J. Ind. Eng. Chem.*, 1913, **5**:35), has pointed out that a clear humus filtrate may be secured by shaking the mixture of soil and ammonia, pouring as much soil as possible on the filter and returning the filtrate to the filter until it begins to run through clean.

By this procedure it has been found possible to obtain a clear filtrate from all the soils tested. The filtrate, however, contains mineral matter which may be precipitated by means of ammonium carbonate. The liquid sometimes appears clear after the ammonium carbonate is added, but, when filtered, the precipitate is easily seen on the filter paper, and the filtrate contains a smaller amount of ash.

The following method was used in some comparative tests made by J. B. Rather, of the Texas Agricultural Experiment Station:

Digest 10 grams of the soil, washed with 1 per cent hydrochloric acid and water, with 500 cc. of 4 per cent ammonium hydroxid, shaking frequently, for 24 hours (8 a.m. to 8 a.m.). Shake the mixture well and pour the entire amount on double fluted 24 cm. S and S filters No. 597. Pour back on the filter the solution which has run through the filter, catch the filtrate in an Erlenmeyer and place the funnel directly in the flask; invert 9-inch evaporating dishes over the funnel to check

evaporation, complete the determination as in the official method, using an aliquot taken from the filtrate (after filtering 24 hours). In no case does a sediment form in solutions on long standing, indicating that the ammonium carbonate precipitate is colloidal.

TABLE 3.

Determination of humus by Smith method.

SOIL	HUMUS		ASH	
	In clear filtrate	After precipitation	In clear filtrate	After precipitation
	per cent	*per cent*	*per cent*	*per cent*
114	0.47	0.52	0.35	0.20
2835	1.21	1.17	0.83	0.26
3335	0.86	0.83	0.28	0.21
6187	3.42	3.08	2.48	0.33
823	0.85	0.75	1.12	0.28
823	0.97	0.81	1.40	0.34
978	1.16	1.03	1.05	0.70
1203	0.84	0.71	1.06	0.34
Average	1.22	1.11	1.07	0.33

Conclusion.

A clear humus filtrate may be obtained by the method of transferring soil to filter as proposed by Smith, but the filtrate contains colloidal mineral matter which is precipitated by ammonium carbonate.

BEAM METHOD.

A study was made of the Beam (*Kairo Sci. J.*, May, 1912) method for humus, the important points of which consist in washing the soil with a solution of carbon dioxid after the extraction with acid, and in reprecipitating the ammonium carbonate precipitate. The method as tested is described as follows:

Preparation of filter.—Provide a No. A Büchner funnel with a paper disk which will act as a support for a thin, well-distributed layer of asbestos. Carry out the suction with the filter pump until the asbestos is comparatively dry.

Extraction of lime.—Mix 10 grams of soil with about 10 grams of well-extracted fine quartz and distribute in an even layer over the filter with a camel's hair brush. Add a layer of sand and cover the whole with a disk of filter paper. Pour 1 per cent hydrochloric acid through the filter until the filtrate is free from lime, then remove the acid by washing with a cold saturated solution of carbon dioxid. The above operations should be carried out without the use of the filter pump.

Extraction of humus.—Pour successive small portions of 4 per cent ammonia on the filter until the filtrate comes through colorless (about fifteen washings were required in the work by the referee); make up the filtrate to 500 cc. with 4 per cent ammonia. Complete a portion as described and treat another portion as follows:

Reprecipitation of clay.—Precipitate the clay with 0.5 gram of ammonium carbonate as usual from 100 cc. of the humus solution prepared as just described. Filter

on an 11-cm. filter, place the filter and precipitate in a beaker, and digest for a few minutes with about 50 cc. of warm ammonium hydroxid. Remove the filter, reprecipitate with about 0.5 gram of ammonium carbonate, and filter, adding the filtrate to the original filtrate from the clay. Complete as usual.

NOTE: In routine analyses 6 grams of soil and a volume of 300 cc. would be sufficient. Mr. Rather reports as follows on the method:

TABLE 4.
Determination of humus by official and Beam methods.

SAMPLE	HUMUS		ASH	
	Beam method	Official method	Beam method	Official method
	per cent	*per cent*	*per cent*	*per cent*
2469	0.86	0.69	0.40	0.36
2477	1.51	1.48	0.78	0.70
2948	1.25	1.10	0.30	0.33
4638	1.10	1.10	0.40	0.46
Average	1.18	1.09	0.47	0.46

I consider the method impracticable on soils of the character used, because of the length of time necessary to complete the determinations. The extraction of lime was readily accomplished by the Beam method which in this respect is quite satisfactory. The passage of the carbonated water through the soil, at first rapid, soon became very slow. The effect of the carbon dioxid was practically lost, because the water had ample time to lose nearly all of that gas before it passed through the soil. Suction of any sort caused a complete cessation of the filtration. The time necessary for the continuous washing varied from about one week to a month. On two samples the washings were not completed at the end of about 1½ months and were then discarded. In this respect the method appears to be as unsatisfactory as the official method. Washing with the ammonia wash was, in most cases, quite slow, but better than with water. Gentle suction was found to be practicable, but about a week was required for complete extraction (15 washings). Attention is called to the fact that, by long contact with ammonia, organic matter, not ordinarily soluble in ammonium hydroxid might be rendered soluble. The reprecipitation of the clay required a little more time than when the clay was not so treated. When the ammonia extract of the filter and clay were warmed with a little ammonium carbonate no difficulty was had in reprecipitating the clay.

Conclusion.

It is believed by the referee the removal of the lime by washing on a filter under a filter disk, the removal of the acid by washing with successive portions of carbonated water in a closed bottle or cylinder, the subsequent extraction of the humus by the official method, and the completion by ammonium carbonate and reprecipitation, would form a satisfactory method.

WHITE METHOD.

W. H. McIntire has called attention to the work of J. W. White at the Pennsylvania Agricultural Experiment Station, in which the soil was

placed on filter paper in a Büchner funnel, and there washed with the acid and with water. The acid and wash water were placed in an inverted bottle, so as to feed automatically.

This method gave very unsatisfactory results in tests made by Mr. Rather. The soils tested required 2 to 30 hours for washing with acid, and from 3 hours to 41 days for washing with water. The filter paper clogged with some of these soils.

OTHER METHODS.

From some of our previous work with humus, it has seemed possible that the action between the acid and the humate is reversible, and thus, although an excess of acid may be present, all the humate is not decomposed by a single treatment with acid. In order to test this point, several experiments were made, as follows:

One series of 10 grams of soil was digested for 24 hours at room temperature with fifth-normal hydrochloric acid. This should be sufficient to dissolve 11.2 per cent of lime in such quantity of soil. Another series of soils was digested twice with the acid, and still another series three times. A portion (20 cc.) of the acid was titrated with tenth-normal caustic soda after each extraction. The soil was washed thoroughly after the extractions were complete, extracted with 4 per cent ammonia, and the determination completed by the ammonium carbonate method.

The results are given in Table 5. With soils 124 and 324, though only one-fourth of the acid was used by the soil, a second extraction with

TABLE 5.

Determination of humus by extractions with acid.

SOIL NO.	HUMUS			HUMUS ASH			ACID NOT NEUTRALIZED		
	Digestions			Digestions			Digestions		
	1	2	3	1	2	3	1	2	3
SERIES I:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*cc.*	*cc.*
114	0.57	0.47	....	0.20	0.22	....	37.2	40.5	....
124	2.77	3.18	....	0.45	0.65	....	35.1	40.2	....
142	1.60	1.59	....	0.45	0.32	....	39.2	40.6	....
324	1.95	2.25	....	0.71	0.90	....	33.0	40.5	....
326	0.67	0.64	....	0.20	0.19	....	39.0	39.6	....
845	1.98	2.08	....	0.33	0.37	....	37.0	40.2	....
Average	1.59	1.70	....	0.39	0.44	....	36.8	40.3	....
SERIES II:									
110	0.63	1.45	1.73	0.47	0.59	0.47	12.7	35.6	37.6
324	0.13	0.52	1.22	0.16	0.36	0.39	0.0	8.4	33.6
330	0.21	1.66	1.98	0.19	0.41	0.35	1.4	26.4	36.4
331	0.25	2.32	2.76	0.18	0.53	0.40	0.7	24.1	35.8
338	0.42	0.96	1.23	0.31	0.43	0.41	6.8	33.9	37.4
933	0.28	0.95	1.09	0.38	0.43	0.40	4.4	34.0	37.4
Average	0.32	1.31	1.67	0.28	0.46	0.40	4.3	27.1	36.4

acid increased the quantity of humus and humus ash. The soils of the second series contain more lime than the first series. It is seen that, though all the acid was not used on some of them, the second extraction with acid increased decidedly the quantity of humus dissolved, and the third extraction showed a decided increase over the second, though a large proportion of the acid was not used.

Conclusions

From these results it is believed that a method for humus in which there is only a single extraction with acid would not be satisfactory. It should, however, be possible to devise one with two extractions which should be sufficient, provided that the first extraction took out almost all the lime.

RECOMMENDATION.

The referee makes the following recommendation:

That the Rather modification for the method for humus be adopted as official.

Sufficient study has been given to this method to show that it is simple and accurate. The method now official is not accurate. The use of the Rather method is a step forward in the improvement of the method. Some other method may possibly later be found more exact or accurate, but the method now official and inaccurate should be displaced by one which is more nearly correct.

DIFFERENCES IN LIME REQUIREMENT AS INDICATED BY THE VEITCH METHOD.

By A. W. Blair and H. C. McLean.

It is the purpose of this paper to consider not the Veitch method in comparison with other methods for determining soil acidity, but rather the results obtained by this method with samples of soil from limed and unlimed plots, and with samples from plots that have received different quantities of lime. In connection with pot and cylinder experimental work on the availability of nitrogenous fertilizer materials, which has been carried on at the New Jersey Agricultural Experiment Station for some years, two field experiments were started in 1908.

EXPERIMENT I.

One experiment was planned for the study of the relative availability of nitrogenous materials, and was also arranged to show the effect of lime as compared with that of no lime. There are forty plots, one-

twentieth acre in size, designated as "1 A" to "20 A" and "1 B" to "20 B." The twenty plots marked "A" have received no lime, while the twenty marked "B" were limed at the rate of one ton of ground limestone per acre in 1908. The majority of these plots receive the nitrogen annually in the same amounts, but in different forms. A few of the plots, however, receive no nitrogen and others receive rather excessive amounts. Sixteen plots in each section receive the following treatment, namely, acid phosphate at the rate of 640 pounds and potassium chlorid at the rate of 320 pounds, per acre, annually. Certain check plots receive no fertilizers whatever, and others receive no nitrogen.

A five-year rotation, consisting of corn, oats, oats, wheat, and grass, has been used. A careful record has been kept of the nitrogen applied, the dry weight of the crop, and the percentage of the applied nitrogen that has been recovered in the crops for the five years beginning with the corn crop of 1908. When these results were brought together, it was found that the corn was better on the limed than on the unlimed plots, both the yield and the percentage of nitrogen recovered being greater on the former than on the latter. After the first year, however, there was practically no difference in the crops from the two sections, the yields of dry matter, the percentage of nitrogen recovered, and the percentage of nitrogen in the dry matter, being practically the same.

Since the crops employed in this rotation have usually responded to the use of lime, it was thought that the failure in this case might be the result of a failure to apply enough lime when the experiment was started. Consequently, at the close of the first rotation and before lime was again applied, samples of the soil were collected from all plots and the lime requirement determined by the Veitch method. The results are indicated in Table I.

From the table it may be seen that all the plots were acid at the time the samples were collected in 1913, the unlimed showing a lime requirement varying from 1400 to 2200 pounds per 2,000,000 pounds of soil, and the limed a lime requirement varying from 1000 to 1500 pounds per 2,000,000 pounds of soil. In two or three instances, at least, there appears to be a relationship between the nitrogen treatment and the lime requirement. Plots 5 A and 6 A, which receive annually manure at the rate of 16 tons per acre, show a high lime requirement; Plots 8 A, 8 B, 9 A, and 9 B, which receive nitrate of soda at the rate of 160 and 320 pounds per acre, respectively, show a low lime requirement; Plots 11 A and 11 B, which receive ammonium sulphate, show a high lime requirement; Plots 12 A and 12 B, which receive calcium cyanamid, show a low lime requirement. The moderately low requirement of Plots 18 A and 20 A may be due to the annual application of nitrate of soda in connection with the manure and green wheat.

TABLE I.

Lime requirement of soil from unlimed and limed plots.

PLOT NO.	FERTILIZER TREATMENT	LIME (CaO) REQUIREMENT PER 2,000,000 POUNDS OF SOIL	
		A	B
		pounds	*pounds*
1A 1B	Nothing	1400	1200
2A 2B	16 pounds of muriate of potash	2100	1000
3A 3B	32 pounds of acid phosphate	2100	1000
4A 4B	Minerals[1] only	2100	1100
5A 5B	Minerals + 1600 pounds of cow manure	2100	1200
6A 6B	Minerals + 1600 pounds of horse manure	2200	1500
7A 7B	Nothing	1600	1000
8A 8B	Minerals + 8 pounds of sodium nitrate	1400	1100
9A 9B	Minerals + 16 pounds of sodium nitrate	2100	1000
10A 10B	Minerals + calcium nitrate equivalent to 16 pounds of sodium nitrate	2100	1200
11A 11B	Minerals + ammonium sulphate equivalent to 16 pounds of sodium nitrate	2100	1500
12A 12B	Minerals + calcium cyanamid equivalent to 16 pounds of sodium nitrate	1400	1000
13A 13B	Minerals + dried blood equivalent to 16 pounds of sodium nitrate	2100	1100
14A 14B	Minerals + fish equivalent to 16 pounds of sodium nitrate	2100	1100
15A 15B	Minerals + concentrated tankage equivalent to 16 pounds of sodium nitrate	1800	1200
16A 16B	Minerals + 800 pounds of green alfalfa	2100	1100
17A 17B	Minerals + 800 pounds of green wheat or rye	1600	1100
18A 18B	Minerals + 1600 pounds of cow manure + 16 pounds of sodium nitrate	1600	1200
19A 19B	Minerals only	1400	1100
20A 20B	Minerals + 800 pounds of green wheat or rye + 16 pounds of sodium nitrate	1400	1100
	Average	1840	1140

[1] Minerals = 32 pounds of acid phosphate and 16 pounds of muriate of potash.

Following the timothy crop of 1912, volunteer red clover appeared on nearly all the plots. It was observed, however, that the growth was much heavier on the limed than on the unlimed plots. In order to eliminate any disturbing influence which the clover might have on the nitrogen study, it was decided to dig out the clover as far as possible and this was done in the fall of 1912. The clover was dried and weighed and nitrogen determinations were made. There was about twice as much dry matter on the limed as on the unlimed plots, and the dry matter from the limed plots was distinctly higher in nitrogen than that from the unlimed plots. This seems to be evidence to corroborate the results secured by the Veitch method. The oats, wheat, and timothy, being less susceptible to an acid soil, did not emphasize the differences in acidity; the clover did emphasize these differences.

EXPERIMENT II.

The second experiment was planned to show the amount of lime which should be applied for different crops, and whether there is any difference between the results obtained with magnesian and non-magnesian lime.

TABLE 2.

Lime requirement of soils from plots that have received different quantities of lime

PLOT NO.	SPECIAL TREATMENT	LIME (CaO) REQUIREMENT PER 2,000,000 POUNDS OF SOIL
ROTATION 1	GENERAL FARM CROPS:	
21	Nothing	1200
22	0.5 ton of calcium carbonate per acre	1000
23	1 ton of calcium carbonate per acre	600
24	2 tons of calcium carbonate per acre	000
25	0.5 ton of calcium carbonate + magnesium carbonate per acre	600
26	1 ton of calcium carbonate + magnesium carbonate per acre	700
27	2 tons of calcium carbonate + magnesium carbonate per acre	000
ROTATION 2	GENERAL FARM CROPS AND POTATOES:	
28	Nothing	800
29	0.5 ton of calcium carbonate per acre	800
30	1 ton of calcium carbonate per acre	600
31	2 tons of calcium carbonate per acre	100
32	0.5 ton of calcium carbonate + magnesium carbonate per acre	700
33	1 ton of calcium carbonate + magnesium carbonate per acre	400
34	2 tons of calcium carbonate + magnesium carbonate per acre	300
ROTATION 3	CORN, POTATOES, MARKET GARDEN CROPS:	
35	Nothing	1100
36	0.5 ton of calcium carbonate per acre	800
37	1 ton of calcium carbonate per acre	600
38	2 tons of calcium carbonate per acre	400
39	0.5 ton of calcium carbonate + magnesium carbonate per acre	1100
40	1 ton of calcium carbonate + magnesium carbonate per acre	700
41	2 tons of calcium carbonate + magnesium carbonate per acre	500
ROTATION 4	FORAGE CROPS:	
42	Nothing	1200
43	0.5 ton of calcium carbonate per acre	1100
44	1 ton of calcium carbonate per acre	700
45	2 tons of calcium carbonate per acre	600
46	0.5 ton of calcium carbonate + magnesium carbonate per acre	1100
47	1 ton of calcium carbonate + magnesium carbonate per acre	500
48	2 tons of calcium carbonate + magnesium carbonate per acre	300

For this experiment 28 one-twentieth acre plots were arranged in 4 sections (to accommodate as many rotations) of 7 plots each. The first plot in each section is the check plot, while the second, third, and fourth received in 1908 0.5, 1 and 2 tons, respectively, of finely-ground non-magnesian limestone, and the fifth, sixth, and seventh received similar amounts of magnesian limestone. The plots in any particular rotation received a uniform fertilizer treatment, consisting of acid phosphate, potassium chlorid and dried blood (with the market garden crops nitrate of soda was also used). Samples of soil were collected from these plots at the end of the rotations and the lime requirement determined by the Veitch method. The results of these determinations are shown in Table 2:

Although five crops have been harvested from these plots, the influence, on the soil, of the lime which was applied in 1908 is clearly shown by the lower lime requirement. On the other hand, the crop returns for these five years would, if tabulated, show an upward trend as the amount of lime was increased.

Extreme accuracy can not be claimed for this method. Differences of 100 or 200 pounds of lime, or ground limestone, per acre, will make little difference in actual practice. The results of these experiments do, however, seem to make it certain that the method may be depended upon to show differences in lime treatment within reasonable limits, and that it may, therefore, be used as a safe guide in determining the amount of lime to be applied for different crops.

METHOD FOR DETERMINING THE LIME REQUIREMENT OF SOILS.

By C. H. Jones.

To 5.6 grams of soil, add 0.5 gram of calcium acetate (tested reagent), place in a 3-inch mortar and mix with pestle; add sufficient water (room temperature) to make a fairly stiff paste, pestle for 20 seconds, add 30 cc. of water and continue the mixing for 30 seconds. Wash into a 200 cc. flask and keep bulk down to about 160 cc.; let stand with occasional shaking for 15 minutes; make up to bulk of 200 cc., mix, and filter through a dry filter; discard first 10 to 15 cc. which may be cloudy. Titrate 100 cc. of the clear filtrate, using phenolphthalein as an indicator with tenth-normal sodium hydroxid. This reading multiplied by 2 gives the number of cubic centimeters of tenth-normal alkali required to neutralize the acetic acid in 200 cc. of the solution. This figure times the factor 1.8 times 1000 equals the pounds of lime (CaO) required per 2,000,000 pounds of soil.

The factor 1.8 is a tentative one only, it having been secured on a rel-

atively small number of samples representing Rhode Island, Massachusetts, Vermont, and New Jersey soils. The method is extremely rapid, one man easily making 50 determinations in a day.

F. P. Veitch.—I would like to refer to the determination of the lime requirements of soils, and again point out the necessity of using in this work, pure distilled water free from alkalies and acids, and vessels which are not soluble in water; vessels in which 100 cc. of the distilled water when evaporated nearly to dryness with a few drops of phenolphthalein solution does not become pink. Results reported from time to time seem to show that the analysts have used water that is not pure or glassware which is affected by the distilled water. Possibly their distilled water is prepared from a steam boiler supply in which an alkaline boiler compound is used. I do not believe that where one analyst reports a lime requirement of 1200 parts per million, and another that the same soil is alkaline, the results should be blamed upon the lime water method. While I have no definite results on the point, I am confident however, that the lime requirements of a soil varies from time to time throughout the year. I have examined samples which at one time were decidedly acid and at other times were possibly alkaline. This is a matter that needs more consideration than it has received in the past. These variations are due perhaps to the time of year the sample is taken, perhaps to improper sampling, or to the inclusion in one of the samples of particles of undecomposed lime.

THE EFFECT OF THE PRESENCE OF AMMONIUM CARBONATE UPON HUMUS DETERMINATIONS.

By W. H. McIntire and J. I. Hardy.

At the 1912 meeting of this association, P. F. Trowbridge, of Missouri, cited work done in his laboratory by O. C. Smith on a gravity filtration method for the determination of humus (*J. Ind. Eng. Chem.*, 1913, **5**: 35). The method consists of transferring the suspended soil to gravity filters and returning the filtrate until it becomes clear. By permitting filtration to occur during the day, the filtrate is perfectly clear by night, and enough of the solution is secured overnight to accomplish the determination. Subsequent to this announcement the authors tried filtration by transferring the agitated soil solution, substituting the perforated disk of the Büchner funnel for the gravity filter, and using suction. It was found that in this way a battery of 10 solutions could be filtered during a day, approximately 100 cc. passage of solution being required to clarify the filtrate thoroughly. This was not sufficiently rapid to accomplish the large number of determinations required, and the Rather method (Texas Agricultural Experiment Station Bul. 139) was modified by filtering immediately after 36 hours' digestion with 4 per cent ammonia, 2.5 grams of ammonium carbonate being introduced into the cylinder at the time of filtration.

With but slight mixing, which was found superior in speed of filtration to vigorous shaking, the entire solution was thrown upon Büchners with

suction, and the passage of but 15 cc. of solution was required to clarify the filtrate thoroughly. The introduction of ammonium carbonate so hastened the clarification and so increased the speed of filtration that 50 filtrations of 250 to 300 cc. were made upon a battery of 10 filters in a day. This procedure eliminates the time necessary to await precipitation of clay as in the Rather method. The average of 102 determinations on the same soil by the Rather method gave an ash content of 0.33 per cent, varying from 0.24 per cent to 0.52 per cent, while an average of 81 determinations by the modification gave an ash content of 0.18 per cent, with variations of from 0.11 to 0.24 per cent. Furthermore, upon standing

Effect of different amounts of ammonium carbonate, introduced into ammonia upon humus determinations, and influence of period of contact of soil with solution.

SOIL	METHOD OF TREATMENT	TIME OF CONTACT WITH AMMONIUM HYDROXID	HUMUS				ASH			
			A	B	C	Average	A	B	C	Average
		hours	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Loam	Straight filtration.	36	1.29	1.20	1.38	1.29	0.53	0.53	0.62	0.56
do	do	192	1.25	1.31	1.28	1.28	0.37	0.37	0.37	0.37
do	2.5 grams of carbonate in contact.	36	0.98	0.99	1.09	1.02	0.15	0.15	0.21	0.17
do	do	192	1.09	1.10	1.09	1.09	0.16	0.18	0.17	0.17
do	2.5 grams of carbonate at time of filtration. . .	36	1.03	1.05	1.17	1.08	0.18	0.18	0.21	0.19
do	do	192	1.30	1.29	1.31	1.30	0.21	0.18	0.20	0.20
do	2.5 grams of carbonate in contact.	36	0.77	0.80	0.87	0.81	0.12	0.13	0.18	0.14
do	do	192	0.86	0.87	0.88	0.87	0.16	0.14	0.15	0.15
Virgin meadow soil	Straight filtration. . . .	36	4.35	4.28	4.36	4.33	0.53	0.67	0.81	0.67
do	do	192	4.90	4.88	4.89	4.89	0.91	0.95	0.88	0.91
do	2.5 grams of carbonate in contact.	36	3.87	3.87	4.00	3.91	0.41	0.39	0.40	0.40
do	do	192	4.21	4.11	4.18	4.17	0.34	0.36	0.35	0.35
do	2.5 grams of carbonate at time of filtration . .	36	3.44	3.49	3.93	3.62	0.33	0.38	0.31	0.34
do	do	192	5.12	4.92	4.94	4.99	0.86	0.87	0.82	0.85
do	2.5 grams of carbonate in contact.	36	2.62	2.60	2.81	2.68	0.25	0.29	0.29	0.28
do	do	192	3.18	3.14	3.12	3.15	0.23	0.27	0.22	0.24

several months the solution by the Rather method gave a precipitate, while none occurred in the solution obtained by the modified procedure. In 18 instances analyses were made of the solution obtained immediately after addition of ammonium carbonate and filtration, and compared with 18 determinations made upon second filtrations obtained by filtering the residue which had remained in contact with ammonia and ammonium carbonate for 8 to 10 days. An average of the 18 determinations of the first filtrations gave 1.18 per cent of humus, while an average of 18 determinations on the second filtration gave 1.40 per cent. This seemed to point to greater solvent action of the ammoniacal solution subsequent to introduction of the carbonate, or to an introduction of the factor of time of contact. To throw light upon the observation, the scheme given in the table on page 45 was tried, and the results obtained thereby are shown to demonstrate the action of ammonium carbonate.

The color of the solutions and the data of the table show undoubted occlusion or precipitation of humus or decreased solubility by the ammonium carbonate in the small amounts, and still greater in the larger amounts. In other words, the occlusion is dependent upon the amounts of ammonium carbonate present. On standing for periods of from 8 to 10 days, the amount of humus dissolved by the solutions containing carbonate was increased considerably over the contact period of 36 hours. If the introduction of carbonate be permissible, the determinations should all be run upon filtrate secured at the same time, or upon new filtrates secured by repetition of the method, and not upon the residues which have been in contact with the soil residue for longer periods.

Investigations on the chemical and physical effects produced by the introduction of ammonium carbonate into an ammoniacal solution of humus are to be reported in detail in Tennessee Agricultural Experiment Station Bulletin 103.

HUMUS DETERMINATIONS.

By O. C. Smith.

At the meeting last year the Missouri Agricultural Experiment Station reported some results on humus determinations, using a slight modification of the official method (see *J. Ind. Eng. Chem.*, 1911, **3**: 660; 1913, **5**: 35). In this modification the sample digested with the 4 per cent ammonium hydroxid is thoroughly shaken and all the material immediately transferred to a dry filter. The turbid filtrate is returned to the filter, keeping the filter well filled until the filtrate becomes clear. The time required is from 2 to 12 hours. In November of last year G. S. Fraps, of the Texas Agricultural Experiment Station kindly sent us some samples of soil which gave poor results by the official method, and one of them

failed to give satisfactory results by the Rather modification. By the official method it was impossible to obtain a clear filtrate with these soils.

The following table gives the results obtained upon these soils by three of the methods proposed, and for comparison the results on one reported by J. B. Rather, of the Texas station.

Determination of humus by three methods.

METHOD	12-11-145 (5974)		12-11-146 (5975)		12-11-147 (6187)	
	Humus	Ash	Humus	Ash	Humus	Ash
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Smith	2.15	0.31	1.00	0.43	3.81	2.00
	2.07	0.72	0.82	0.48	3.66	2.86
	2.15	0.78	1.00	0.49	3.74	3.93
	....	....	....	....	3.82	2.26
Average	2.12	0.60	0.94	0.46	3.76	2.76
Rather by Smith	1.81	0.27	0.88	0.41	7.14	24.01
	1.97	0.30	0.96	0.46	6.29	17.86
Average	1.89	0.28	0.92	0.43	6.72	20.93
Official by Smith	3.58	11.55	2.16	10.78	7.93	33.29
	4.00	11.76	2.58	13.21	8.20	35.01
Average	3.79	11.65	2.37	11.99	8.07	34.15
Official,[1] (by Rather)	....	....	....	....	7.31	34.80
Rather[1] (by Rather)	....	....	....	....	5.13	17.20
Modified Rather (by Rather)	....	....	....	....	2.73	0.14

[1] *J. Ind. Eng. Chem.*, 1913, **5**: 222.

These three samples were transferred to the filter at 11 o'clock and by 2 o'clock sufficient clear filtrate (100 cc.) was obtained from two of the samples. From the third, No. 6187, (a Hawaiian soil furnished Mr. Fraps by Kelley and McGeorge of the Hawaiian Station), 100 cc. of clear filtrate were obtained at 6 o'clock. In this sample the Rather method yielded 20.93 per cent of ash, and with our modification 2.76 per cent. Correspondingly, the humus by the Rather method is 6.72 per cent and by our modification is 3.76 per cent, or a decrease of 1 per cent in ash gives a decrease of 0.16 per cent in humus, due in all probability to a dehydration of the ash. On this same soil the Rather method compared with the Huston-McBride method reduces the ash from 34.15 per cent to 20.93 per cent, the humus being reduced from 8.07 to 6.72 per cent, or a reduction of 0.103 per cent of humus for each 1 per cent of ash, due to dehydration of the ash. From Mr. Rather's data on this same soil (*J. Ind. Eng. Chem.*, 1913, **5**: 222) when comparing the results obtained by the official method with those obtained by his proposed method

it is found that his method reduces the ash from 34.80 per cent to 17.20 per cent, and the humus from 7.31 per cent to 5.13 per cent, or a reduction of 0.12 per cent in the humus for each per cent of ash. The modified Rather method reduces the ash on this soil from 17.20 per cent to 0.14 per cent, and the humus from 5.13 per cent to 2.73, 1 per cent of ash equaling 0.14 per cent of humus. An average of the results of the four comparisons shows that in this soil a reduction of 1 per cent in the ash means a reduction of 0.13 per cent in the humus, due to the dehydration of the ash.

If, now, the results obtained on this soil by the Smith method be compared with those reported by Mr. Rather obtained by using his proposed modification which consists in adding 2 grams of ammonium carbonate to the filtrate and heating on the steam bath 1 hour, it is found that he has reduced the ash from 2.76 per cent to 0.14 per cent and that he has reduced the humus from 3.76 per cent to 2.73 per cent. In thus reducing the ash and the humus to a minimum for each per cent of ash reduced he has decreased the humus 0.39 per cent or a total reduction in humus of 1.03 per cent. Considering the average figure obtained above, allowing a reduction of 1 per cent of ash to cause a decrease of 0.13 per cent of humus, due to dehydration of the ash, it is found that the 2.62 per cent decrease in ash should give a decrease of 0.34 per cent of humus, while Mr. Rather obtains a decrease of 1.03 per cent in humus. His results, therefore, are lowered 0.68 per cent due to the action of the ammonium carbonate or to the heating.

Kelley and McGeorge (*J. Ind. Eng. Chem.*, 1912, **4**: 664) have shown that ammonium carbonate even when added in very small quantities precipitates some of the humus and in the work of this station comparing the Rather method with our own method it has been observed that the filtrate from the Rather method was always lighter in color. Alway, Files, and Pickney (Nebraska Agricultural Experiment Station Bul. 115) have shown that by decreasing the concentration of the ammonium hydroxid solution, less humus is dissolved. Heating a 4 per cent ammonium hydroxid solution on the water bath for one hour will very likely drive off some of the ammonia.

After the determinations were made on the three soils 250 cc. of each were put into graduated cylinders and allowed to stand undisturbed. After one month Sample 5974 showed 25 cc. of clear solution, Sample 5975, 20 cc., and Sample 6187, 10 cc. After more than one year in 5974 there were 225 cc. of clear solution, in 5975, 180 cc., while in 6187 there were only 50 cc. and this solution was not as clear as the filtrate obtained by our method.

Thus it may be seen that the official and original Rather methods are wholly inadequate for this last soil and the modified Rather method introduces too many doubtful factors.

REPORT ON NITROGENOUS COMPOUNDS IN SOILS.

By J. K. Plummer, *Associate Referee.*

In compliance with a resolution passed by the association at its 1912 meeting a study of the colorimetric methods used in determining nitrogenous materials in soils has been undertaken. As nitrates are the most important compounds under consideration, and as there have been pointed out sources of error in the methods commonly used for their estimation, it was thought best to take up the question of nitrates first.

The well-known phenoldisulphonic acid method is the one in general use for the colorimetric estimation of nitrates. Two modifications of this method have been proposed: That offered by Gill[1] many years ago and the one worked out by Chamot[2] and his associates.

The work this year has consisted of a comparison of these two modifications, and an attempt to evolve a method which could be used satisfactorily for the clarification of the water extract for the nitrate determinations, Lipman and Sharp[3] having shown the clarification agents in common use, carbon black and aluminum cream, to be worthless for the purpose intended.

As lime has been used satisfactorily by these investigators to free the solution of clay and organic matter and by the North Carolina Station[4] in the work in soil bacteriology since 1908 to test its efficiency along with the Chamberland-Pasteur filter, the following directions were sent out.

The amounts of lime to be used were different for the several collaborators, to ascertain the amount which would be required to coagulate the clay content of the average soil, the greater part of the excess being removed by carbon dioxid. With these directions was sent a sample of loam soil upon which the nitrate content had been determined several hundred times.

INSTRUCTIONS FOR COÖPERATIVE WORK.

PREPARATION OF SOIL EXTRACTS.

Shake for 2 hours 100 grams of soil with 200 cc. of distilled water. Allow the sand and coarse silt to settle and draw off 100 cc. or more of the suspension, to which add from 0.5 to 3 grams of c. p. lime (the amount varied with the collaborator), heat slightly, and pass a stream of carbon dioxid through the solution until all the lime has been converted to the bicarbonate; boil off the excess of carbon dioxid and filter through a fluted filter, care being taken that the loss in volume due to boiling be made up with distilled water, or the original suspension be forced through a Chamberland-Pasteur filter, discarding the first 75 cc. which passes through the tube.

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[1] *J. Amer. Chem. Soc.*, 1894, **16**: 122.

[2] *J. Amer. Chem. Soc.*, 1911, **33**: 366.

[3] Univ. Calif. Bul., vol. **1**, no. 2, pp. 21-37.

[4] *Centrbl. Bakt.*, 1909, **23**: 357.

Gill modification.

Preparation of the phenoldisulphonic acid reagent.—Mix 3 grams of pure crystallized phenol with 37 grams (20.1 cc.) of sulphuric acid (specific gravity 1.84) and heat for 6 hours at 100°C. by letting the lightly-stoppered flask rest in boiling water. The acid thus prepared may crystallize out on standing, especially during cold weather. It may be brought back into solution by heat; the addition of water for solution should be avoided.

Analytical process.—Evaporate 50 cc., or any convenient volume of the solution clarified as given, to dryness on water bath, removing dish as soon as completely dry. Add 1 cc. of the disulphonic reagent, prepared as directed by Gill, and stir with a glass rod. The time of contact between reagent and nitrate residue should be 10 minutes. Dilute with distilled water, and make alkaline with ammonium hydroxid (strong ammonia, specific gravity 0.9 diluted with an equal volume of water). Then dilute to 50 or 100 cc. and compare with standard treated similarly. Should the color be too intense for direct readings an aliquot portion may be taken and diluted to a definite volume, and the strength of this determined. Should chlorids be present in appreciable amounts they may be removed by solid silver sulphate free from nitrates.

Withers and Stevens[1] have shown that all the nitrate can not be removed from soils by shaking with water, and the amount of recovery bears a relation to the amount present. With this in mind, each collaborator was requested to determine by both modifications the amounts which could be removed from the soil alone, and to add a known amount of nitrogen as c. p. potassium nitrate to see how much could be recovered by both modifications.

RESULTS OF COLLABORATION.

The following table gives the results as obtained by the different chemists who used the lime method.

TABLE 1.

Determination of nitrates by the lime method and by the Chamberland-Pasteur filter.

METHOD AND ANALYST	NITRIC NITROGEN						
	In soil		Added	Recovered		Recovered	
	Gill	Chamot		Gill	Chamot	Gill	Chamot
LIME METHOD:	*parts per million*	*parts per million*	*parts per million*	*parts per million*	*parts per million*	*per cent*	*per cent*
G. W. Walker, Minnesota	11.60	11.50	...	...	...	...	...
	11.60	11.50	...	...	...	...	...
Average	11.60	11.50	...	...	...	...	...
G. W. Walker, Minnesota	...	...	100.00	91.4	93.5	91.4	93.5
C. B. Lipman, California	12.80	12.00	...	...	...	...	...
	12.00	12.00	...	...	...	...	...
	11.52	12.48	...	...	...	...	...
	11.20	12.00	...	...	...	...	...
	12.00	12.22	...	...	...	...	...
	12.22	12.00	...	...	...	...	...
	12.00	12.30	...	...	...	...	...
	11.36	12.18	...	...	...	...	...
Average	11.88	12.15	...	...	...	...	...

[1] *Centralbl.*, 1910, **25**: 75.

TABLE 1—Continued.

Method and analyst	Nitric nitrogen: In soil, Gill	In soil, Chamot	Added	Recovered, Gill	Recovered, Chamot	Recovered, Gill	Recovered, Chamot
	parts per million	*parts per million*	*parts per million*	*parts per million*	*parts per million*	*per cent*	*per cent*
LIME METHOD:							
L. L. LaShell, Ohio	14.52	14.52	...	...	...	...	...
	12.71	13.38	...	...	...	...	...
Average	13.61	13.95	...	...	...	...	...
L. L. LaShell, Ohio	...	...	13.86	13.54	14.89	97.7	107.5
C. J. Schollenberger, Ohio	10.35	14.52	...	...	...	...	...
	10.71	13.38	...	...	...	...	...
Average	10.53	13.95	...	...	...	...	...
J. K. Plummer, North Carolina	11.40	12.50	...	...	...	...	...
	11.60	12.80	...	...	...	...	...
	11.00	12.50	...	...	...	...	...
	11.40	12.20	...	...	...	...	...
Average	11.35	12.50	...	...	...	...	...
J. K. Plummer, North Carolina	...	...	100.00	96.80	97.80	96.8	97.8
	...	...	100.00	96.00	98.10	96.0	98.1
	...	...	50.00	47.90	48.00	95.8	96.0
	...	...	25.00	23.10	24.20	92.4	96.8
Average	...	...	...	...	...	95.3	97.2
C. J. Schollenberger, Ohio	10.10	10.00	...	...	...	...	...
	...	11.90	...	...	...	...	...
	10.70	11.90	...	...	...	...	...
	11.90	12.20	...	...	...	...	...
Average	10.90	11.60	...	...	...	...	...
C. J. Schollenberger, Ohio[1]	...	...	100.00	105.30	107.20	105.3	107.2
Total average	11.64	12.58	...	...	...	97.4	101.4
CHAMBERLAND-PASTEUR FILTER:							
A. L. Feild, North Carolina	10.55	10.55	...	...	...	...	...
	10.62	10.55	...	...	...	...	...
Average	10.58	10.55	...	...	...	...	...
A. L. Feild, North Carolina	...	...	41.60	34.90	42.06	83.9	101.1
	...	...	41.60	...	40.38	...	97.1
Average	...	...	...	...	41.22	...	99.1
H. C. McLean, New Jersey	6.27	6.55	...	...	...	...	...
	...	...	300.00	174.00	182.00	58.0	60.7

[1] After the addition of lime, soil was centrifuged instead of filtered.

DETERMINATION OF NITRATES.

Chamot-Pratt Modification.

Preparation of the phenoldisulphonic acid reagent.—Dissolve 25 grams of pure phenol in 150 cc. of pure concentrated sulphuric acid, add 75 cc. of fuming sulphuric acid (13 per cent of SO_3), stir well, and heat for 2 hours at about 100°C.

Analytical process.—To 50 cc. or any convenient volume depending on the nitrate content, of the solution clarified as above, add sufficient 0.04 normal sulphuric acid to nearly neutralize the alkalinity; then if chlorids are present in appreciable amounts, a volume of nitrate-free silver sulphate solution to remove the chlorin. Heat to boiling and add a small amount of aluminum cream, filter, and wash 6 or 8 times with small amounts of hot water. Evaporate to dryness, add 2 cc. of the disulphonic reagent prepared according to the directions given by Chamot, rubbing with a glass rod to ensure complete contact. Should the residue be compact or vitreous due to much iron or magnesium, place on water bath for 5 minutes. Dilute with distilled water and slowly add sufficient potassium hydroxid solution (10 to 12 normal) until the maximum color has been produced. Transfer to colorimeter cylinder, filtering if necessary, and compare with a potassium nitrate standard treated with 2 cc. of this reagent.

A comparison of the results obtained with the lime method for the clarification of the suspension and those obtained with the Chamberland-Pasteur filter as the clarifying agent, would tend to show that there is a marked absorptive power possessed by the filter for nitrates, as all the determinations, except those made by Feild with the Chamot modification when 41.6 parts per million of nitric nitrogen were added, are lower than the results obtained with lime. As several of the collaborators had reported absorption in this way, the experiment was tried of running a standard potassium nitrate solution through the filter and making the determinations of nitrate after passing the filter. To clean the tube 100 cc. of distilled water were forced through first. The results are given in the following table:

Determination of nitrates in a standard potassium nitrate solution.

NO.	PORTION WHICH PASSED THROUGH TUBE	PARTS PER MILLION OF NITRIC NITROGEN RECOVERED
SOLUTION CONTAINING 10 PARTS PER MILLION OF NITRIC NITROGEN:		
1	Last 30 cc. portion of distilled water	0.0
2	First 30 cc. of nitrate solution	3.4
3	Next 25 cc. of nitrate solution	5.6
4	Next 50 cc. of nitrate solution	6.8
5	Next 75 cc. of nitrate solution	7.5
6	Next 200 cc. of nitrate solution	8.9
SOLUTION CONTAINING 100 PARTS PER MILLION OF NITRIC NITROGEN:		
1	Last 30 cc. of distilled water	0.0
2	First 25 cc. of nitrate solution	39.4
3	Next 25 cc. of nitrate solution	44.7
4	Next 50 cc. of nitrate solution	64.7
5	Next 75 cc. of nitrate solution	77.3
6	Next 180 cc. of nitrate solution	93.9

The use of aluminum cream is questionable as shown in the following results on a sample of soil sent out:

Determination of nitrates by Chamot-Pratt method.

ANALYST	NITRIC NITROGEN	
	With aluminum cream	Without aluminum cream
	parts per million	*parts per million*
C. B. Lipman	11.12 10.56 10.08 10.88	12.00 12.00 12.20 12.00
Average	10.66	12.05
J. K. Plummer	11.80 12.00 11.60 11.00	12.20 11.85 12.40 12.00
Average	11.60	12.11

COMMENTS BY COLLABORATORS.

C. B. Lipman: For the clarification of soil extracts, I am inclined to the use of the lime method without the carbon dioxid step. The excess of lime causes little or no trouble and its removal with carbon dioxid causes the loss of time and may give rise to a loss of nitrate. In some preliminary work with the Chamberland-Pasteur filter losses of nitrate were observed when the whole 200 cc. of suspension were forced through the tube. When 2 cc. of the freshly-prepared disulphonic acid under Gill's directions are used, the results are about the same as with the Chamot reagent. The latter, however, without aluminum cream, gives higher results. It entails more trouble in its preparation.

A. L. Feild: While the Chamot reagent is undoubtedly more scientifically prepared and gives more uniform colors to match with the standard, the Gill method offers some advantages. With the latter method, less reagent is used, consequently a smaller volume of the yellow solution can be obtained, and in soils having a low nitrate content more satisfactory readings can be obtained.

G. W. Walker: It appears to me that the Gill method of procedure in the analytical process is better, as it gives about as good results and is shorter. The Chamot method for the preparation seems to give a reagent of more uniform color than the Gill.

L. L. LaShell: The Gill method is more easily carried out at the point of developing color, as potassium hydroxid gives crystals which separate out and larger volumes of yellow solution must be taken for comparison. This will make it difficult to read soils which have a low nitrate content. Volume of solution is too small to permit filtering through Chamberland-Pasteur filter.

C. J. Schollenberger: The Chamot modification appears to give higher and more consistent results than the Gill, but it will be difficult to read with soils low in nitrate, due to volume of solution necessary to dissolve the crystals which separate on the addition of potassium hydroxid. Five-tenths of a gram of lime is not enough to coagulate the clay content of this sample; it requires from 1 to 2 grams. Boiling off the excess of carbon dioxid causes solution of some of the humus, giving

foreign color. Removal of excess of lime is not necessary. After the addition of lime the centrifuge offers a good means of removing the clay. The Chamberland-Pasteur filter absorbs too large a proportion of nitrate to allow its use for this purpose.

H. C. McLean: I am inclined to use the Gill method of procedure, as it is shorter and gives about as good results. The color produced by the Chamot reagent has a more uniform color to deal with than that of Gill's reagent.

CONCLUSIONS.

It would seem from a comparison of the results that lime is the best agent known for the clarification of soil extracts in which the nitrate determinations are to be made. The absorptive power possessed by the Chamberland-Pasteur filter tube would tend to debar this piece of apparatus for this work.

The amount of lime necessary for the removal of clay varies in different soils, but 2 grams are about all that are needed for 100 grams of most loam soils. It can be added to the soil itself, so as to have it present in the shaking process, or better after the shaking, by drawing off the suspension and adding the lime to this, shaking at intervals for 30 minutes.

The Chamot modification, except in two instances (Walker and Feild), gave higher results than the Gill method on the soil alone, and in every instance in which potassium nitrate was added. The agreement between the analysts on the soil alone was remarkably close when lime was used. When the Chamberland-Pasteur filter was used for the clarification there was not such agreement. While Feild's results on the soil alone were in fair agreement, they were lower than the average for the lime method, and his results after the addition of potassium nitrate are decidedly varying. The results obtained by McLean are much lower than the lime method. He says, however, that he did not shake continuously, but at intervals, which may be the cause of the variance in his results. The use of aluminum cream as recommended by Chamot is questionable, but the fact that this method gives higher results in every instance in which potassium nitrate was added, and in every instance except two on the soil alone is significant. That this reagent is more scientifically prepared and that the color produced from it is more satisfactory to match with the standard can hardly be disputed.

RECOMMENDATIONS.

It is recommended—

(1) That the reduction method for the determination of nitrates in soils be studied, as the colorimetric method is worthless in the case of "alkali soils."

(2) That the colorimetric methods for the estimation of nitrites and ammonia be studied.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By W. H. McIntire, *Referee*, and B. E. Curry, *Associate Referee.*

The association at its 1912 meeting directed a further study of the Schreiber method for total sulphur as given in Bureau of Chemistry Circular 56, and additional study of its official method for ferric oxid and aluminum oxid as extended to the determination of calcium and magnesium. The work on sulphur was done under the direction of the associate referee, to whom credit is due for the work here reported upon samples of bran and linseed meal.

COMPARISON OF THE SCHREIBER AND SODIUM PEROXID METHODS FOR TOTAL SULPHUR.

Determination of total sulphur in bran and linseed meal.

METHOD AND ANALYST	TOTAL SULPHUR	
	Bran	Linseed meal
Schreiber method:	*per cent*	*per cent*
Firman Thompson, Newark, Del.	0.754	1.026
	0.541	1.103
	0.514	1.011
	0.739	1.131
	0.611	1.046
	0.709	.....
Average	0.645	1.063
Maximum variation	0.240	0.120
G. E. Boltz, Wooster, Ohio	0.711	1.029
	0.691	1.033
	0.707	1.041
	0.684	1.029
	0.679	1.061
	0.692	.....
Average	0.694	1.039
Maximum variation	0.032	0.032
H. Rosenthal, Columbia, Mo.	0.746	1.151
	0.634	1.116
	0.634	.....
	0.674	.....
Average	0.672	1.134
	0.112	0.035
A. J. Patten, East Lansing, Mich.	0.713	1.114
	0.706	1.084
Average	0.710	1.099
Maximum variation	0.007	0.030
Grand average	0.680	1.084
Sodium peroxid (official) method:	.....	1.063
	.....	1.108
Average	.....	1.086

Although an official procedure has been adopted for total sulphur determinations, the technique of the method as carried out by A. J. Patten, of Michigan, is so simple and satisfactory that his letter of transmittal is here given for the benefit of the association:

For comparison, results are given on linseed meal by the sodium peroxid method, which I consider superior to the Schreiber method in that it is simpler and does not introduce so many factors that may disturb the precipitation of barium sulphate. The sodium peroxid method is very simple, and when carried out in the manner described should give no trouble.

Sodium peroxid (official) method.—Weigh the substance into a nickel crucible of 150 or 200 cc. capacity, add 10 cc. of water, and stir; then place the crucible in a pan of cold water and add slowly 5 grams of sodium peroxid stirring with a platinum rod. (If the crucible is kept cool no difficulty is experienced in adding the peroxid.) Place the crucible on the hot plate and allow to remain until the contents are perfectly dry; again add 5 grams of sodium peroxid, and place the crucible covered tightly over the free flame and bring the contents to complete fusion. For the first 5 minutes it is well to have the flame just touching the bottom of the crucible, after which the full flame may be turned on.

Sodium peroxid free from sulphur may be obtained without difficulty. Results reported by Mr. Schreiber in Circular 56 of the Bureau of Chemistry are in almost every case slightly higher by the peroxid method than by the proposed method, and, moreover, the peroxid method may be conducted with very much less attention to details than may the Schreiber method.

In view of the excellent results secured by twelve analysts upon the present official method and reported to the association at its 1910 meeting, at which time the method was officially adopted, the referee would state that he heartily concurs in the opinion of Mr. Patten, and since no object seems to be attained by duplication of methods very similar, he would recommend that no further work be done on the Schreiber method.

CALCIUM OXID AND MAGNESIUM OXID DETERMINATIONS.

The favorable results of the preceding referee and of the present referee on the proposed extension of the official method for iron and aluminum to include the determination of calcium and magnesium, where the usual minute quantities of manganese are present were responsible for the further work on this extension during the past year. It was intended to study any interference of large occurrences of manganese. The calcium was precipitated from the large volume resulting from the washing of iron and aluminum precipitate before elimination of manganese. It was found necessary to follow this procedure because the concentration of the solution under either acid or ammoniacal conditions resulted in the precipitation of calcium molybdate. By the usual redissolving and reprecipitation of the calcium oxalate, minute quantities of manganese were occluded from the abnormal occurrence of this element. Though the occluded manganomanganic oxid is sufficient to color the precipitate,

it was found as an average of 6 determinations by the referee to amount to only 0.4 mg. O. B. Winter, of Michigan, tested the calcium oxid precipitate and found 0.3 mg. of manganomanganic oxid, and J. P. Aumer, of Illinois, found 0.0019 mg. of manganomanganic oxid as an average of 8 determinations. It was the sense of the subcommittee passing upon 1912 recommendations that the minute occurrences (and oftentimes absence) of manganese would not vitiate any results within the most exacting margin of analytical error. If the normal occurrences of manganese were occluded in the same proportion as the abnormal amounts, by percentage, the occluded oxid could not be determined. The method used by Mr. Winter for determining the trace of manganomanganic oxid was not given. Mr. Aumer determined the oxid by direct and indirect removal of manganese with ammonium persulphate and by bromin precipitation, while the referee dissolved the calcium oxid with very dilute nitric acid and weighed the remaining manganomanganic oxid. The procedure outlined is as follows:

EXTENSION OF OFFICIAL MOLYBDIC METHOD FOR IRON AND ALUMINUM TO INCLUDE DETERMINATION OF MANGANESE, CALCIUM, AND MAGNESIUM.

Keep the filtrate and washings from the first and second precipitations of iron and aluminum hydroxids to a volume of 500 cc.; add ammonia and ammonium oxalate, redissolve the precipitate and reprecipitate as in calcium in soils (Bul. 107, Rev., p. 15). Then acidify the combined filtrates and washings from calcium determination and evaporate them to crystallization in a porcelain casserole. Place the casserole under a hot plate, protected from falling particles, and expel the ammonium salts.

Take up with a few cubic centimeters of hydrochloric acid and water and filter off molybdic acid, washing the precipitate until it is free from chlorin. Bring the filtrate to volume of 100 cc., and add 1 or 2 drops of concentrated bromin. Make alkaline with ammonia and permit to stand several minutes without agitation. Filter off the precipitated manganese without boiling, wash, ignite, and weigh the precipitate as manganomanganic oxid. Concentrate the alkaline filtrate from the manganese separation to 75 cc. and precipitate magnesium as in soils (Bul. 107, Rev., p. 16). Then dissolve this precipitate in hydrochloric acid and reprecipitate as above, filter, ignite and weigh as magnesium pyrophosphate.

RESULTS OF COLLABORATION.

Calcium oxid and magnesium oxid recovered from aliquots of 50 cc. of synthetic plant ash solution.

ANALYST	CALCIUM OXID (27 DETERMINATIONS)		MAGNESIUM OXID (17 DETERMINATIONS)	
	grams	*per cent*	*grams*	*per cent*
O. B. Winter, East Lansing, Mich.	0.0560		0.0463	
	0.0554		0.0459	
	0.0558		0.0457	
	0.0564		......	
	0.0560		......	
	0.0559		......	
Average	0.0559		0.0460	
Maximum difference	0.0010		0.0006	
G. E. Boltz, Wooster, Ohio	0.0547		......	
	0.0550		......	
	0.0550		......	
	0.0551		......	
Average	0.0550		......	
Maximum difference	0.0003		......	
S. R. Mitchell, State College, N. M.	0.0595		0.0480	
	0.0593		0.0476	
	0.0610		......	
Average	0.0599		0.0478	
Maximum difference	0.0017		0.0004	
J. P. Aumer, Urbana, Ill.	0.0539		0.0451	
	0.0547		0.0475	
	0.0567		0.0490	
	0.0563		0.0477	
	0.0581		0.0485	
	0.0550		0.0486	
	0.0566		0.0459	
	0.0560		0.0466	
Average	[1]0.0559		0.0474	
Maximum difference	0.0042		0.0039	
W. H. McIntire, Knoxville, Tenn.	0.0556		0.0454	
	0.0567		0.0451	
	0.0568		0.0454	
	0.0576		0.0443	
	0.0545		......	
	0.0558		......	
Average	[1]0.0563		[1]0.0451	
Maximum difference	0.0031		0.0011	
Grand average	0.0566	11.32	0.0466	9.32
Amount present	0.0569	11.38	0.0465	9.30
Error	−0.0003	−0.06	+0.0001	+0.02

[1] CaO purified.

COMMENTS BY ANALYSTS.

O. B. Winter: With proper care the method seems quite accurate.

E. Van Alstine, for J. P. Aumer: I may say that by following the directions as given, when the calcium oxid was weighed it was colored by the presence of manganese. After being weighed, it was redissolved, the manganese removed, and the calcium again precipitated and weighed as calcium oxid, it being white this time.

S. R. Mitchell: Too much risk of loss of material by volatilization with ammonia fumes, by spurting out. Believe that some way should be suggested to avoid accumulation of so much ammonium salt.

CONCLUSIONS.

The results secured by the coöperators are remarkably close, differing from theory by 0.3 mg. as an average of 27 determinations for calcium oxid and 0.1 mg. in the case of magnesium oxid as an average of 17 determinations.

In view of the excellent results secured by the method during four years of study, and the slight occlusion of manganese even when its occurrence is made many times that of normal, the referee recommends the adoption of the method as provisional, with a view to its being made official.

It is suggested, in conclusion, that if considered essential, purification of the calcium oxid precipitate be accomplished by solution of the lime by very dilute nitric acid, which does not attack the manganomanganic oxid. In this way occluded manganomanganic oxid may be easily and rapidly determined and correction made therefore.

At 12.45 the convention adjourned until 2 p.m.

MONDAY—AFTERNOON SESSION.

At the opening of the afternoon session the president appointed the following committees:

Committee to invite the Secretary of Agriculture and the Assistant Secretary to address the association: W. A. Withers, of North Carolina; L. L. Van Slyke, of New York, and F. T. Shutt, of Canada.

Committee on nominations: R. J. Davidson, of Virginia; J. W. Kellogg, of Pennsylvania; and C. S. Cathcart, of New Jersey.

Committee on resolutions: J. M. Bartlett, of Maine; A. W. Blair, of New Jersey; and E. W. Magruder, of Virginia.

Auditing committee: J. P. Street, of Connecticut; H. D. Haskins, of Massachusetts; and W. H. McIntire, of Tennessee.

REPORT ON INSECTICIDES.

By S. D. Averitt, *Referee.*

The work on insecticides for the past year, in accordance with the recommendations of the association has included a comparison of the methods for the analysis of lime-sulphur solutions proposed by the referee for 1911 with those proposed by the present referee in 1912, and a comparison of the method of digestion of lead arsenate for water-soluble arsenic proposed by the present referee, with the provisional 10 days'

digestion. The work on lime-sulphur solutions has required so much time that the second proposition has received very little attention.

LIME-SULPHUR SOLUTIONS.

For the comparison of the methods for the analysis of lime-sulphur solutions, two samples of known composition were made and sent out about the middle of February, 1913, to fifteen chemists who agreed to assist in this work.

Two solutions, A and B, were used in making the samples of lime sulphur. A was a lime-sulphur solution made by boiling for 45 minutes in an atmosphere of hydrogen 100 grams of Kahlbaum's calcium sulphid (CaS), 150 grams of precipitated sulphur, and one liter of distilled water. The calcium sulphid was tested for other metals and none were found. B was a solution of calcium thiosulphate which had no trace of sulphid. These solutions were very carefully analyzed, duplicates run in all cases, and in the case of A, both the iodin method and the zinc chlorid method were employed in the determination of thiosulphate sulphur in order that there might be no question raised as to the accuracy of that determination and both methods gave the same figure. The following table gives the results of that work:

Solution A.

TOTAL SULPHUR	MONOSULPHUR EQUIVALENT	THIOSULPHATE SULPHUR	SULPHATE SULPHUR	LIME (CaO)
per cent	*per cent*	*per cent*	*per cent*	*per cent*
12.22	2.33	0.59	0.09	4.69
12.21	2.35	0.59	0.09	4.71
Average, 12.22	2.34	0.59	0.09	4.70

Thiosulphates by zinc chlorid method: 0.57, 0.60, and 0.59 per cent; average, 0.59 per cent.

Solution B.

TOTAL SULPHUR	THIOSULPHATE SULPHUR	SULPHATE SULPHUR	LIME (CaO)	
			Determined	Calculated
per cent	*per cent*	*per cent*	*per cent*	*per cent*
5.42	5.37	0.08	4.82	4.85
5.46	5.37	0.08	4.84	......
Average, 5.44	5.37	0.08	4.83	......

As stated before, B was entirely free of sulphids. It was tested with both nickel sulphate and sodium nitroprussid. Sample 1 was made by adding to exactly 500 grams of A, exactly 500 grams of freshly-boiled and cooled distilled water. Sample 2 was made by adding to exactly 500 grams of A exactly 500 grams of B. These samples were kept bottled several weeks before transferring to the sample bottles sent to the workers.

Assuming that no change had taken place in the solutions, Sample 1 should have had the following composition: Total sulphur 6.11 per cent, thiosulphate sulphur 0.30 per cent, monosulphur equivalent 1.17 per cent, sulphate sulphur 0.05 per cent, lime (CaO) 2.35 per cent, sulphid sulphur (by difference) 5.77 per cent. Sample 2 should have had the following composition: Total sulphur 8.83 per cent, thiosulphate sulphur 2.99 per cent, monosulphur equivalent 1.17 per cent, sulphate sulphur 0.09 per cent, lime (CaO) 4.77 per cent, sulphid sulphur 5.77 per cent.

INSTRUCTIONS FOR COÖPERATIVE WORK.

Dear Sir: I am sending you by parcel post 2 samples of lime-sulphur solutions made carefully by myself; their composition is definitely known.

The referee for 1911 holds that the methods proposed last year are not accurate and that those proposed by him in 1911 are so, and the association instructed that the methods be compared. The methods proposed in 1912 are those worked out by J. E. Harris at the Michigan Agricultural Experiment Station and published in Technical Bulletin No. 6 of that Station, with some changes in detail and manipulation which were found to facilitate the work. The methods of 1911 (Bur. Chem. Bul. 152, p. 70) may be called the zinc chlorid methods, and those proposed last year (Bur. Chem. Bul. 162, pp. 36–37) the iodin methods, for distinction.

My objections to the zinc chlorid methods are based on the 1911 figures and on other work done by myself. The method for total sulphur is too indefinite and in the hands of an inexperienced worker may lead to bad results; the method for sulphid sulphur involves the filtering and washing of zinc sulphid, is long and tedious, and did not give accurate results on the 1911 samples; the method for thiosulphate sulphur did not give accurate results on the 1911 samples; the figures for sulphate sulphur in 1911 are not correct. The former referee denies that these objections are valid. The work of a half dozen good chemists this year, however, should settle the question.

I believe the zinc chlorid methods will give better results this year than in 1911 because the samples submitted this year offer better conditions for good results. I have found sodium peroxid a better oxidizing agent than hydrogen peroxid; it does the work in a fraction of the time and can be obtained sulphur free.

I desire to call attention to the determination of lime (CaO). Many of the results last year were not correct. I regretted it very much as the lime affords the only check upon the analysis of a straight lime-sulphur solution as ordinarily made. The samples submitted this year are of such strength that 10 grams should be made to 100 cc. and 10 cc. aliquots used for the determinations in the iodin methods. Freshly-boiled and cooled distilled water should be used for this work in both methods.

Do not fail, after having done the work, to give me your opinion of the methods. An analyst's comments are often of nearly as much value to the referee as his figures, in that they show the advantages and disadvantages of a method which figures alone do not reveal.

I think no change will take place in the samples, but it will be best to do the work as soon as you can find time for it. They should be protected from the air as much as possible during the work. Report results as soon as work is done. Your work will be very much appreciated.

RESULTS OF COLLABORATION

Reports have been coming in from 13 of the chemists assisting in this work since about March 1.

Comparison of the iodin and zinc chlorid methods for the analysis of lime sulphur solutions.

Sample 1.

ANALYST	TOTAL SULPHUR		SULPHID SULPHUR		THIO-SULPHATE SULPHUR		SULPHATE AND SULPHITE SULPHUR		MONO-SULPHUR EQUIVALENT	TOTAL LIME (CaO)		SULPHID SULPHUR BY DIFFERENCE
	Sodium peroxid	Hydrogen peroxid	Iodin	Zinc chlorid	Iodin	Zinc chlorid	Iodin	Zinc chlorid	Iodin	Determined	Calculated	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. W. Gaither, Wooster, Ohio	6.20	6.12	5.85	5.45	0.38	0.32	0.05	....	1.21	2.32	2.32	5.76
	6.12	6.01	5.78	[1]5.19	0.32	0.26	0.05	....	1.19	2.31	[2]2.46	[2]5.72
	6.15	6.08	5.82	[1]5.28	0.35	0.30	0.04	0.06	1.20	2.34	.	....
	6.15	6.10	5.81	[1]5.26	0.35	0.32	0.04	....	1.20	2.32	....	....
	6.13	6.08	5.81	[1]5.37	0.35	0.32	....	....	1.20	2.32	..	....
O. B. Winter, Geneva, N. Y.	6.15	6.19	5.98	5.73	0.24	0.26	0.04	0.03	1.22	2.36	2.41	5.86
	6.15	6.16	5.86	5.58	0.27	0.27	0.04	0.04	1.22	2.28	[2]2.45	[2]5.36
	6.14	....	5.94	5.82	0.24	.	0.04	.	1.21	2.38	.	....
G. P. Gray, Berkeley, Calif.	5.98	6.14	5.92	5.80	0.24	[1]0.18	0.04	0.02	1.19	2.27	2.35	5.81
	6.14	6.08	[1]6.04	5.85	0.24	[1]0.18	0.03	[1]0.01	1.18	2.21	[2]2.30	[2]5.91
	6.11	..	...	...	0.24	...	...	..	1.21	....	...	....
	6.10		.		[1]0.18		.	...	1.19	...	....	....
D. M. Nelson, Chicago, Ill.	6.03	6.01	5.48	5.86	0.33	[1]0.15	[1]0.08	0.02	1.16	2.21	2.44	5.65
	6.16	6.24	[1]5.26	5.87	0.35	[1]0.14	[1]0.08	0.03	1.17	2.20	[2]2.17	[2]5.97
	5.99	6.14	...	5.90	0.34	[1]0.12	0.06	..	1.16	2.18	...	....
			...	5.92	0.36	[1]0.12		..	1.12	...	....	....
A. J. Patten, and W. C. Marti, East Lansing, Mich.	6.13	6.16	5.73	5.73	0.26	0.22	0.03	0.03	1.18	2.37	2.35	5.84
	.		.	...	..	.	..	..	....	2.36	[2]2.31	[2]5.91
S. D. Averitt, Lexington, Ky.	6.07	6.12	5.82	5.85	0.29	0.26	0.05	0.03	1.18	2.38	2.39	5.80
	6.19	6.13	5.89	5.91	0.26	0.29	0.05	0.03	1.16	2.34	[2]2.38	[2]5.82
	6.13		5.77		0.29	0.28	0.04	...	1.18	2.35	.	....
	6.13				0.26	...	..	..	1.18	2.34	...	....
	.		...	.	0.29	....	...	...	1.18	2.34	...	....
H. H. Hill, R. J. Davidson, W. B. Ellett, H. O. Tillman, Blacksburg, Va.	6.10	6.15	....	....	0.26	0.39	[1]0.01	0.03	1.15	2.52	2.33	5.89
	6.18	6.23	....	....	0.26	0.39	[1]0.01	....	1.15	2.54	[2]2.48	[2]5.81
	6.12	6.24	....	....	0.29	....	....	....	1.15	2.52	....	....
	6.22	6.25	....	....	0.29	....	....	....	1.22	2.52	....	....
	6.16	....	....	....	0.26	....	....	....	1.21	...	....	....
	6.24			.	0.26	....	..	..	...	....	....	....
	.	.		..	0.26	.	...	...	.	....	....	....
W. J. Morgan, Washington, D. C.	5.93	6.22	5.40	5.99	[1]0.49	0.25	0.07	0.03	1.14	2.22	2.56	5.46
	6.07	...	[1]5.30	5.84	[1]0.45	[1]0.18	[1]0.09	0.02	1.14	2.24	[2]2.27	[2]5.98
			5.45	.	[1]0.45		..	.	1.15	2.22	..	....
			5.60	.	.	...	.	...	1.15	2.27	...	....
			5.46	.	...		.	..	1.15	..	...	....
R. C. Roark, Washington, D. C.	6.15		[1]6.18	..	[1]0.52	0.22	[1]0.08	.	1.11	2.22	2.45	5.61
	6.18		[1]6.08	.	[1]0.56	[1]0.17	0.07	..	1.12	2.23	[2]2.20	[2]5.94
			5.99		[1]0.42		0.07	.	1.15	..	...	...
		.		.	[1]0.46		0.06	.	1.15	..	...	....
	...			.	.	.	0.06	..	.	...	....	....
General average	6.13	6.14	5.77	5.81	0.29	0.29	0.05	0.03	1.17	2.32	2.42	5.74
Theoretical	6.11		5.77	...	0.30		0.05	....	1.17	2.35	[2]2.34	[2]5.88

[1] Not included in the general average.
[2] Calculations using the zinc chlorid figures for thiosulphate sulphur and sulphate sulphur.

Sample 2.

ANALYST	TOTAL SULPHUR		SULPHID SULPHUR		THIO-SULPHATE SULPHUR		SULPHATE AND SULPHITE SULPHUR		MONO-SULPHUR EQUIVALENT	TOTAL LIME (CaO)		SULPHID SULPHUR BY DIFFERENCE
	Sodium peroxid	Hydrogen peroxid	Iodin	Zinc chlorid	Iodin	Zinc chlorid	Iodin	Zinc chlorid	Iodin	Determined	Calculated	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. W. Gaither, Wooster, Ohio	8.90	8.81	5 95	5.42	3.07	2.94	0.08	0.08	1.18	4.82	4.85	5.74
	8.84	8.78	5.65	[1]5 09	3.01	2.82	0.07	0.08	1.18	4.84	[2]4.67	[2]5.82
	8 87	8.70	5 81	[1]5.24	3.06	2.86	0.08	0.04	1.18	4.83	....	....
	8.86	8.66	5.80	[1]5.26	3.07	2.88	0.06	0.05	1.18	4.83	....	....
	8.84	....	5 86	[1]5.36	3.07	2.85	....	....	1.18	....	....	....
O. B. Winter, Geneva, N. Y.	8.83	8.78	5.98	5.60	3.00	2.98	0.05	0.07	1.22	4.77	4.83	5.79
	8.86	8.83	5.94	5.53	2.98	2.96	0 06	0.12	1.22	4.79	[2]4.92	[2]5.73
	8.84	....	5.76	5.74	2.99	2.99	....	....	1.22	4.77	....	....
	....	.	....	....	2.99	....	....	....	1.22	....	....	....
G. P. Gray, Berkeley, Calif.	8.67	8.45	5.86	5.82	3.02	2.69	0.07	0 05	1 17	4 44	4 82	5.61
	8.63	8 46	5.83	5.83	3.02	2.75	0.06	0 06	1.17	4.69	[2]4 53	[2]5.68
D. M. Nelson, Chicago, Ill.	8.72	8.70	[1]6.33	5.70	3.02	2.77	0.15	0.10	1.15	4.70	4.89	5.54
	8.70	8.74	[1]5.19	5.69	3.02	2 84	0.13	0.05	1.15	4.70	[2]4.60	[2]5.84
	8.69	8.76	[1]4.31	5.65	3.06	2.83	0.13	....	1.13	4.72	....	....
	....	....	....	5.67	....	2.79	....	....	....	....	....	....
	....	....	....	5.75	....	....	....	....	....	...	....	....
A. J. Patten and W. C. Marti, East Lansing, Mich.	8.81	8.79	5.85	5.83	2.94	[1]2.58	0.07	0.05	1.15	4.70	4.70	5.80
	....	....	.	....	.	. .	....	....	....	....	[2]4.36	[2]6.16
S. D. Averitt, Lexington, Ky.	8 82	8 73	5 92	5 84	2 99	3 00	0 10	0.05	1 17	4 77	4 83	5.77
	8 85	8 67	5 88	5 88	2 97	2 94	0 09	0 06	1 18	4.79	[2]4.75	[2]5.67
	....	....	....	...	2 99	2 97	0.09	....	1 18	4.82	....	....
	...	.	...	...	2 94	2 96	....	....	1 17	....	....	....
	.		..	..	2 99	....	....	....	1 18	....	....	....
H. H. Hill, R. J. Davidson, W. B. Ellett, H. O. Tillman, Blacksburg, Va.	8.71	8 91	....	....	3.01	3.09	0.12	0.10	1.14	4.84	4.87	5.67
	8.91	8.85	....	....	3.07	[1]2.56	0.11	0.11	1.14	4.83	[2]4.88	[2]5.97
	8.88	8.92	....	....	3.07	....	0.11	....	1.17	4.88	....	....
	....	....	....	....	3.07	....	0.12	....	1.17	5.12	....	....
	....	....	....	....	....	....	....	....	1.17	....	....	....
	.	.	..	.	.	....	....	....	1.12	....	....	....
W. J. Morgan, Washington, D. C.	8.81	8.90	5.70	[1]6.06	[1]3.12	[1]2.63	0.11	0.05	1.16	4.61	4.96	5.53
	8.84	8.94	5.43	[1]6.17	[1]3.20	[1]2.63	0.10	0.06	1.13	4.63	[2]4.39	[2]6.23
	....	....	....	....	[1]3.23	....	....	....	1.13	4.68	....	....
	....	...	...	...	[1]3.23	....	....	....	1.14	4.70	....	....
	..	...	....	..	...	....	....	....	1 13	....	....	....
R. C. Roark, Washington, D. C.	9.00	....	5.72	....	[1]3.14	[1]2.48	0.09	...	1 15	4 65	4 95	5.77
	....	....	5.90	....	[1]3.20	[1]2.54	0.09	...	1 17	4 64	[2]4.35	[2]6 42
	. .	...	5.84	....	3 05	....	0.09	....	1.18	....	....	....
	....	...	5.87	....	[1]3.11	....	0.10	....	1.18	....	....	....
	....	.	5.78	....	....	....	0.09	....	....	....	....	....
	....	. .	....	....	....	....	0.12	....	....	....	....	....
General average	8.81	8.76	5.82	5.77	3.02	2.89	0.09	0.07	1.17	4.75	4.86	5.69
Theoretical	8.84	....	5 77	....	2 99	....	0 09	....	1 17	4.77	[2]4.61	[2]5.95

[1] Not included in the general average.
[2] Calculations using the zinc chlorid figures for thiosulphate sulphur and sulphate sulphur.

COMMENTS OF ANALYSTS.

E. W. Gaither: Since I have not had any extended experience with the analysis of insecticides, I do not feel free to criticize the two methods very extensively. I will say, however, that judging from my results, the iodin method seems the more accurate. From the standpoint of ease and speed of manipulation it is preferable.

O. B. Winter: (1) Sodium peroxid as used in the iodin method seems to be the better oxidizing agent. Its use saves time, and it can be obtained sulphur-free more easily than can hydrogen peroxid. (2) There should be no difficulty in getting the end point when titrating with iodin for either the monosulphid or thiosulphate sulphur in the iodin method, and this method is much more convenient than the zinc chlorid method. (3) The iodin method for estimating sulphate and sulphite sulphur gives agreeing results, while the zinc chlorid method does not. In Sample 1 the results agree in both methods and with each other but in Sample 2 the zinc chlorid method gives widely-varying results. When the solution is heated the results are likely to run high. (4) The check on the work by calculating the lime (CaO) that is combined with the different forms of sulphur is a great advantage. (5) In estimating the sulphid sulphur, the iodin method does away with the device for removing clear test portions in order to get the end point when adding ammoniacal zinc chlorid. Getting this end point is tedious. Filtering and washing the free sulphur in the iodin method is done much more easily than filtering and washing the zinc sulphid. (Here I find it advantageous to allow the free sulphur to stand in the solution for several hours, stirring it occasionally to remove from the sides and bottom of the containing vessel. This overcomes the stickiness that sometimes exists, and it filters clear without difficulty.) In general, I believe the iodin method for analyzing lime-sulphur solutions is more accurate than the zinc chlorid method, and it is more convenient.

G. P. Gray: (1) *Total sulphur.*—From the experience in this laboratory on these and other samples, equally accurate results are obtained by either method. The method of oxidation with sodium peroxid seems decidedly preferable on account of greater rapidity and the elimination of the blank. (2) *Sulphid sulphur.*—Little preference is shown in either of the methods where the direct determination is made. (3) *Iodin titration.*—The results seem to give somewhat high figures in this work, but it is probable that this could be rectified with more practice in determining the end point. Its simplicity and rapidity certainly commend its use. Suggest taking larger aliquots for titration.

A. V. H. Mory: We found good points and bad points in both the hydrogen peroxid and the sodium peroxid methods for total sulphur. While the sodium peroxid method is shorter, still we were unable to get sodium peroxid from a well-known local supply house which did not contain about one-half as much sulphur as the ordinary commercial hydrogen peroxid obtained without reference to its sulphur content, and the measuring of an exact quantity for the purpose of running a blank was a rather difficult matter. The sodium peroxid was represented to be the best obtainable and contained about 0.03 per cent of sulphur. While our experience with the iodin method for sulphid sulphur was not at all reassuring, we were led to entertain a different sort of opinion of the iodin method in the case of the thiosulphate sulphur and the sulphate sulphur, the manipulation being decidedly rapid and convenient and conducive to concordant results. It is to be noted, however, that the results obtained by the iodin method were higher than by the zinc chlorid method in each case. We do not feel qualified to venture an opinion as to which set of results is nearer the truth. There was little or no difficulty experienced in arriving at an end point in the titration for the monosulphur equivalent.

A. J. Patten: I very strongly favor the Harris methods. They are simpler and much easier of manipulation.

R. J. Davidson: Now, as to any criticism of the iodin method as compared with the official method, I do not feel that I have ever done enough with the method to be in a position to criticize it as it should be done. I think the titration method is certainly a very rapid one, and probably where one has had some experience there will be no difficulty in determining the end point. This, I think, is the chief difficulty that there is with the method, because every excess used here in the monosulphid diminishes the amount of the thiosulphate.

H. H. Hill: We have gone over these methods quite thoroughly and it seems as though the iodin method is superior both in manipulation and accuracy to those proposed by the former referree. Sodium peroxid as an oxidizing agent is much more advantageous, as it can be obtained free from sulphur, while with the hydrogen peroxid much time was required in the preliminary treatment with barium carbonate. Calculating the lime is also another advantage, as it checks the determined lime. With the new method the time of operation is shortened considerably.

R. C. Roark, associate referee: In commenting on these results, I wish first to criticise the samples sent. A good commercial concentrated lime-sulphur solution will contain about 25 per cent of total sulphur, hence your samples do not represent the commercial product, and methods applicable to dilute solutions will not necessarily be suitable for concentrated solutions. The samples sent out were so dilute that they decomposed on standing a few days and solutions made up from them for analysis at the rate of 10 grams to 100 cc. decomposed almost immediately. The monosulphur equivalent may be determined with fair accuracy if the titration is done in a not too dilute solution, but the monosulphur equivalent of itself is a determination of no value. Any error in the monosulphur equivalent titration affects the thiosulphate titration. Furthermore, it affects the amount of sulphur precipitated and hence the sulphid sulphur determination; and there is reason to believe that an excessive amount of iodin may cause an increased formation of sulphates, hence affecting the sulphate sulphur determination. Thus an error in the first titration will make an error in every subsequent determination made on the same aliquot. Results for the thiosulphate sulphur as determined by the Michigan method are of no value due to the titration of hydrosulphid and hydroxyhydrosulphid sulphur as thiosulphate sulphur, as shown by C. C. McDonnell at last year's meeting of the association. Relative to the claim that the lime calculated from the iodin titration agrees with the lime determined, I will say that our analyses of these samples, as well as your analysis of the samples I sent you last May, show that this claim is not supported by the facts. Lime calculated does not agree with lime determined.

DISCUSSION.

Before discussing the results, the referee wishes to call attention to the fact that all but one of the coöperating chemists, in commenting upon the methods, prefer the iodin methods because of the ease and rapidity with which the work is done. One analyst criticizes the samples, regardless of the fact that they favor the methods which he champions. The wording and tone of his criticism, however, convict him of carelessness in handling the samples. He asserts that the monosulphur equivalent of itself is a determination of no value. In the absence of proof to this effect, the use the other chemists have made of it seems to prove the contrary.

His comments in regard to thiosulphate sulphur by the iodin titration method lose much of their force in the face of his figures by the zinc chlorid method, and the figures of the other analysts do not sustain his comments. His comment in regard to the calculated and determined lime is not confirmed by the figures. While the writer is advocating the iodin methods he wants it understood that this is not a personal matter with him, and that he is interested only to the extent that the association will adopt accurate, workable methods. The elimination of some results was in order that neither method should be done an injustice.

As for the results themselves, it should be noted that they show conclusively that dilution has not changed the composition as the average results agree almost perfectly with the theoretical values in all cases except total sulphur and thiosulphate sulphur in Sample 2 by the zinc chlorid methods, and these do not vary much. In all but a few cases in both samples the calculated lime agrees well with the determined lime, the general average of both methods being close to the theoretical in Sample 1 and the iodin figure in Sample 2. The general average of the calculated lime by the zinc chlorid methods in Sample 2 is very low, which fact is explained readily since these values are calculated on each analyst's average, and two or three bad figures in the same direction influence the average. The general average of the sulphid sulphur by difference, by the iodin methods, agrees closely with the theoretical in Sample 1, and fairly well in Sample 2; by the zinc chlorid methods, agrees fairly well in Sample 1 and not well in Sample 2.

The referee has been absolutely fair to both methods in the omission of bad results from the average. It must be noted, however, that the general averages are largely in favor of the iodin methods, notwithstanding the fact that these samples favor the zinc chlorid methods, and the great majority of the chemists get good results by those methods.

REFEREE'S COMMENT ON 1912 PAPER BY McDONNELL.

In a paper entitled "Composition and Methods of Analysis of Lime-sulphur Solutions," read before the last meeting of the association, in opposition to the iodin method, the former referee on insecticides made some statements that subsequent work in my laboratory has shown to be untenable when the experiments upon which he bases his statements are carried on under reasonable conditions.

"The cause of the inaccuracy of the direct iodin titration method" for thiosulphate sulphur he bases upon the work done by Divers and Schimidzu (*J. Chem. Soc.*, 1884, **45**: 270–291). I shall prove to the satisfaction of any disinterested chemist that the statements in this connection are not in accord with the facts as shown by work in my laboratory.

(1) It is claimed that checking the analysis by the determined lime and

the lime calculated from the monosulphur equivalent, the thiosulphate sulphur, and the sulphate and sulphite sulphur, is erroneous because dilution decreases the monosulphur equivalent value and increases the thiosulphate value and that unless the dilution is great the two errors counterbalance each other. Under moderate dilution the monosulphur equivalent is not decreased as I shall show later; neither is the thiosulphate increased. It was the fact that tenth-normal zinc chlorid and tenth-normal iodin gave the same figures for monosulphur equivalent that led Mr. Harris to investigate the direct titration with iodin. Tartar and Bradley of the Oregon Agricultural Experiment Station have shown that standard hydrochloric acid with Methyl Orange as indicator, will give the same value for monosulphur equivalent as standard iodin or standard zinc chlorid. I have corroborated the work of both Harris, and Tartar and Bradley. There is no question about these facts, and if standard zinc chlorid gives the correct sulphid sulphur, standard iodin does also.

Under the head of "Effects of dilution on monosulphur equivalent and thiosulphate" the former referee makes dilutions of 20, 60 and 250 cc. in one case, and 50, 100, and 200 cc. in the other, and for the 250 cc. and 200 cc. dilutions he does have a decreased monosulphur equivalent and an increased thiosulphate figure. Under these dilutions decomposition took place before the titrations could be made. Moreover, in such abnormal dilutions the end points are not distinct. This is self evident when the solution is in the process of breaking down.

Here are the facts in regard to the effect of dilution. From two lime-sulphur solutions, one rather weak and the other much stronger, called for convenience No. 1 and No. 2, I took 20 grams of No. 1 and made it to 100 grams with carbon-dioxid-free water, a dilution of 1 to 4. Of the diluted solution, I took 5 grams, equivalent to 1 gram of original solution and titrated it with twentieth-normal iodin with the following results:

DILUTIONS	IODIN FOR MONOSULPHUR EQUIVALENT	IODIN FOR THIOSULPHATE SULPHUR
cc.	*cc.*	*cc.*
30	12.00	0.75
60	12.00	0.75
100	11.80	0.85

The same treatment of 20 grams of No. 2 gave the following results:

DILUTIONS	IODIN FOR MONOSULPHUR EQUIVALENT	IODIN FOR THIOSULPHATE SULPHUR
cc.	*cc.*	*cc.*
30	16.30	6.50
60	16.30	6.60
100	16.40	6.50

These titrations give in No. 1, 0.96, 0.96 and 0.94 per cent of monosulphur equivalent, and 0.24, 0.24 and 0.27 per cent of thiosulphate; in No. 2, 1.30, 1.30 and 1.31 per cent of monosulphur equivalent, and 2.08, 2.11 and 2.08 per cent of thiosulphate.

It was found that when the dilution amounted to 100 cc. it was necessary to titrate rapidly and use an external indicator for the first end point and starch solution for the other. With dilutions of 150 to 200 cc. the decomposition began so quickly and was so rapid that any values might be obtained depending upon the rate of titration.

When a dilution of 150 to 200 cc. was made with filtered tap water the sulphur would begin to come out by the time it could all be added in 50 cc. portions. In the case of ordinary distilled water there was a short interval between the addition of the water and the precipitation of sulphur. With freshly-boiled and cooled distilled water there was a sensibly longer interval between the addition of the water and the precipitation of sulphur. This indicates that the dilution is not the only factor involved in the decomposition.

From the above figures it appears that any reasonable dilution gives the same values for monosulphur equivalent and thiosulphate sulphur. At the time the above work was being done (February 18, 1913), 20 grams of these samples were made to 100 grams with carbon dioxid free water, bottled, sealed, and left in the laboratory; No. 1 until June 18, 1913, four months later, when the monosulphur equivalent and thiosulphate sulphur were determined by the iodin titration with the following results: Monosulphur equivalent 0.20, 0.20 and 0.20 per cent; thiosulphate sulphur 0.054, 0.054, 0.044 per cent; average monosulphur equivalent 0.20 per cent, average thiosulphate 0.05 per cent, which in the original is equivalent to 1 per cent of monosulphur equivalent and 0.20 per cent of thiosulphate sulphur which is in perfect agreement with what was found in the original four months before.

No. 2 remained in the laboratory until October 13, 1913, eight months after it was made, when the monosulphur equivalent and thiosulphate sulphur were determined as in No. 1 with the following results: Monosulphur equivalent 0.262 and 0.264 per cent; thiosulphate sulphur 0.41 and 0.41 per cent; average monosulphur equivalent 0.263 per cent; average thiosulphate sulphur 0.41 per cent, which in the original is equivalent to 1.32 per cent of monosulphur equivalent and 2.05 per cent of thiosulphate sulphur—a difference of 0.02 per cent in the monosulphur equivalent and 0.04 per cent in the thiosulphate sulphur from the findings in the original eight months before.

As stated before, the dilutions made on the original lime-sulphur solution in order to make the present association samples did not affect the composition, as the work of a large majority of the chemists shows that the

composition of Samples 1 and 2 agrees well with the theoretical values, assuming that dilution made no change in the composition. No further arguments are needed to show that moderate dilution has no effect upon the monosulphur equivalent and thiosulphate content of a lime-sulphur solution. The dilutions made by the former referee are entirely abnormal, and were not contemplated in the instructions for this work.

(2) It is stated upon the authority of Divers and Schimidzu, as noted above, that the inaccuracy of the iodin titrations is due to the fact that there is present in the diluted solution not only calcium polysulphid, calcium thiosulphate, calcium sulphate and sulphite, but calcium hydroxid, calcium hydrosulphid ($Ca(SH)_2$), calcium hydroxyhydrosulphid ($Ca(SH)(OH)$), and hydrogen sulphid (H_2S). Four equations representing the decomposition are given as follows:

$$(1)\ CaS_5+2H_2O=Ca(OH)_2+4S+H_2S$$
$$(2)\ Ca(OH)_2+2H_2S=Ca(SH)_2+2H_2O$$
$$(3)\ Ca(SH)_2+H_2O=Ca(SH)(OH)+H_2S$$
$$(4)\ Ca(SH)(OH)+H_2O=Ca(OH)_2+H_2S$$

It is stated, however, that "These decompositions proceed only when the hydrogen sulphid produced can escape or become diluted." When the first step in this decomposition takes place, which is represented by equation (1), free sulphur must be precipitated. This does not occur unless oxidation takes place which is shown as follows: Many and large dilutions have been made in this laboratory of lime-sulphur solutions with freshly-boiled and cooled distilled water, bottled and sealed at once and allowed to stand in the laboratory for weeks and months and even years, and are as clear in the end as when first made.

There are few solutions more stable than lime-sulphur under any reasonable dilution, provided it is protected from the air or from oxidation in other ways.

To test this decomposition further, two portions of 10 cc. each of a lime-sulphur solution were diluted with 30 cc. of distilled water in a small narrow neck flask and a strip of moistened lead acetate paper suspended above the liquid, the flask stoppered and allowed to stand. At the end of two hours no indication of hydrogen sulphid was visible, at the end of three hours a faint trace was observed, and at the end of four hours it was distinct but the paper was not black, showing that the decomposition proceeds very slowly.

It is stated that the diluted lime sulphur has in addition to the calcium polysulphid and thiosulphate originally present, hydrogen sulphid, calcium hydrosulphid and calcium hydroxyhydrosulphid, all of which form clear solutions and when titrated with iodin the yellow color due to the polysulphids disappears before these colorless sulphur compounds have

been attacked and that they are titrated and calculated as thiosulphate, thus giving a low monosulphur equivalent and a high thiosulphate value. This statement is absurd in the face of the facts shown above. Moreover, if as stated by the former referee, zinc chlorid precipitates the sulphur of these colorless compounds of sulphur (hydrosulphid and hydroxyhydrosulphid) and iodin does not, the average chemist will have difficulty in explaining the fact that standard iodin and standard zinc chlorid give the same values for monosulphur equivalent.

The referee has titrated sodium sulphid (a clear colorless solution) without the use of any indicator at all, and has been able to tell within the limits of experimental error, how much sulphid and thiosulphate sulphur were present in the solution. He has had others mix standard sodium sulphid and standard thiosulphate and upon titrating the solution has determined both very accurately. This is not at all difficult and may be done by any careful analyst. The first addition of iodin will produce a yellow color due to the formation of polysulphid. When this disappears upon further addition of iodin the sulphid sulphur titration is ended. The appearance of the yellow color due to the excess of iodin shows the end of the thiosulphate titration.

As a positive proof that there is no calcium hydrosulphid ($Ca(SH)_2$), or calcium hydroxyhydrosulphid ($Ca(SH)(OH)$) in the solution after the monosulphur equivalent titration with iodin is complete, the writer has repeatedly tested the solution with nickel sulphate and found no sulphids present.

(3) It is stated that the end points in the iodin titrations are not definite, the error in the monosulphur equivalent titration amounting to 0.1 cc. of tenth-normal iodin, and that for the thiosulphate titration being another 0.1 cc., or a total error of 0.2 cc. of tenth-normal iodin, which is asserted by the critic to be a fair degree of accuracy for this titration.

Such errors in the end points will not occur if the directions are followed. An error of 0.05 cc. might be made in the monosulphur equivalent titration as no end point is more definite than that for the thiosulphate titration. The results of a large majority of the workers this year show that this degree of accuracy is not only possible, but that it is very easy to attain. With a little experience the end points are just as definite as that of standard alkali against standard acid with Methyl Orange or phenolphthalein as indicator.

The referee does not claim, however, this definiteness of end points in a lime-sulphur solution so diluted that decomposition begins before the titrations can be made, which will invariably follow dilutions of 150 to 200 cc. as made by the former referee.

(4) In regard to the rapidity of the methods, it is stated that it requires very little more time to make a determination of thiosulphate

sulphur by the zinc chlorid methods than by the direct titration with iodin. To this I will reply that I have made three direct titrations in the time required to make one by the zinc chlorid method. The sulphid sulphur determination by the iodin method requires no more time than by the zinc chlorid and is much easier of manipulation. The comments of the analysts who have aided in the work this year afford a very definite answer to this objection to the iodin methods.

REFEREE'S RESULTS ON COMMERCIAL LIME-SULPHUR SOLUTIONS.

During the past year the referee has had occasion to work upon a half dozen or more samples of commercial concentrates representing the product of four or five of the leading manufacturers of lime sulphur in the country. These samples have been investigated mainly with reference to two points, first, the thiosulphate sulphur as determined by the iodin methods, by the zinc chlorid methods as approved by the association in 1911, and by a modification of the zinc chlorid method as approved; second, the lime as calculated from the iodin titrations and the sulphate and sulphite sulphur compared with the determined lime.

The following facts were found to be true without exception: The thiosulphate sulphur by the zinc chlorid method as approved was always from 0.30 to 0.50 per cent lower than by the iodin method. When, however, 2.5 grams instead of 10 grams were made to 100 c.c. the zinc chlorid method gave results which compared very favorably with the iodin method; when 5 grams were made to 100 cc. the results were intermediate between the figures by the method as approved and the iodin figures. The simplest conclusion to be drawn from these facts is that the thiosulphate is held up by the bulky precipitate of zinc sulphid.

As to the second point investigated, it was found that the lime as calculated from the iodin titrations and the sulphate and sulphite sulphur agrees very closely with the determined lime.

About six weeks ago the referee received from a Kentucky company a sample of their lime-sulphur solution which they are making and selling. They are using a very pure lime and a relatively pure water for this work and the result is a typical straight lime-sulphur solution, a sample of which was sent to the associate referee with the request that he determine by the approved zinc chlorid methods the total sulphur, thiosulphate sulphur, sulphate and sulphite sulphur, and lime. The referee worked this sample by both the iodin and approved zinc chlorid methods and also the thiosulphate sulphur by the zinc chlorid method with 2.5 grams to 100 cc. instead of 10 grams to 100 cc. This work was done in order that the comparison of the two methods might be made complete and that the two points brought out by the referee's work on concentrates as given above might be brought before the association in figures and discussed. The

writer feels that this is the proper and only way to settle the present contention definitely and permanently.

Following is a tabulation of the results:

TOTAL SULPHUR	SULPHID SULPHUR BY DIFFERENCE		MONO-SULPHUR EQUIVALENT	THIOSULPHATE SULPHUR		SULPHATE AND SULPHITE SULPHUR		LIME (CaO)		
								Determined	Calculated	
	Iodin	Zinc chlorid		Iodin	Zinc chlorid	Iodin	Zinc chlorid		Iodin	Zinc chlorid
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
25.80	24.31	24.72	5.03	1.33	1.04	0.17	0.03	10.33	10.27	9.77
			5.03	1.33	1.04	0.16	0.04	10.32		
					1.04					
					2.5 grams to 100 cc.					
					1.30					
					1.30					

Sulphid sulphur: iodin method, $25.80-(1.33+0.17)=24.30$ per cent; zinc chlorid method, $25.80-(1.04+0.03)=24.73$ per cent. Lime (CaO) by calculation, iodin methods $=5.03\times1.75+1.33\times0.87+0.17\times1.75$ or $8.81+1.16+0.30=10.27$ per cent; difference between determined and calculated lime, 0.05 per cent. Lime (CaO) by calculation, zinc chlorid methods $=5.03\times1.75+1.04\times0.875+0.03$ or $8.81+0.91+0.05=9.77$ per cent; difference between determined and calculated lime, 0.55 per cent.

From the above table it will be seen that the calculated lime by the iodin method is in close agreement with the determined lime, there being a difference of only 0.05 per cent. On the other hand the lime calculated, using the zinc chlorid figures for thiosulphate sulphur and sulphate sulphur, and the iodin figures for monosulphur equivalent (standard hydrochloric acid and standard zinc chlorid give the same value as standard iodin for monosulphur equivalent), is 0.55 per cent below the determined value. Now it is perfectly well understood that the calcium and not the sulphur is reacting with the iodin; therefore, the iodin titration is a measure of the calcium combined as polysulphids, and the lime (CaO) equivalent of the calcium (Ca) in the polysulphids plus the lime (CaO) equivalent of the calcium in the thiosulphate, plus the lime (CaO) equivalent of the calcium in the sulphate and sulphite must of necessity be equal to the lime equivalent of all the calcium in the solution. And since in a straight lime-sulphur solution the lime is all in combination as the polysulphids, thiosulphate, sulphate, and sulphite, it follows that the determined and calculated lime must be equal. In the approved zinc chlorid methods the thiosulphate and sulphite figures must be erroneous, because they do not give back the determined lime. The iodin titrations must be right unless

we suppose calcium to exist in a lime-sulphur solution in other combinations than those here considered, and as to this the chemical reactions involved in the making of a lime-sulphur solution preclude the formation of any other compounds. It has been conclusively shown that no change occurs in the solution so long as it is not allowed to oxidize, and any reasonable dilution with carbon dioxid free water produces no change unless oxidation occurs. The inevitable conclusion, therefore, is that the thiosulphate and sulphate sulphur results in a concentrate as determined by the approved zinc chlorid methods, are erroneous.

There is another way to show the inaccuracy of the zinc chlorid methods and the accuracy of the iodin methods, as follows: The sulphid sulphur by the zinc chlorid methods divided by the monosulphur equivalent = $24.73 \div 5.03 = 4.92$, indicating that about 92 per cent of the sulphid sulphur is in the form of calcium pentasulphid. Now, if the sulphur equivalent of the calcium in the polysulphid as shown by the zinc chlorid methods is divided into the sulphid sulphur, $24.73 \div 5.38 = 4.60$, indicating that only 60 per cent of the sulphid sulphur is in the form of calcium pentasulphid. The first ratio indicates an excellent concentrate, the second a rather poor one. Both conditions can not be true, and it is known that this sample is a good concentrate.

On the other hand, the sulphid sulphur, as shown by the iodin methods divided by the monosulphur equivalent, $24.30 \div 5.03 = 4.83$, indicating a good concentrate. The sulphur equivalent of the calcium in the polysulphid as shown by the iodin methods, divided into the sulphid sulphur, $24.30 \div 5.06 = 4.80$, which is entirely consistent with the facts. As stated above, this is a typical lime-sulphur solution and the facts brought out in this discussion were found to be true for all the other samples of concentrates worked.

Last May, following a request for a sample of a commercial concentrate that had been recently worked by the zinc chlorid methods in the Insecticide and Fungicide Laboratory of the Bureau of Chemistry, I received two samples of lime-sulphur solution marked "A" and "B" from the Department of Agriculture. I made the analysis of these samples by the iodin methods as I had proposed to the associate referee for the purpose of comparing the results by the two methods. On account of an error in my first determinations of lime I was led to think they were straight commercial concentrates as my erroneous determinations of lime checked the calculated lime. When the figures by the two methods were compared it was found that on Sample A the zinc chlorid methods gave 0.50 per cent less lime than I found by both calculation and determination by the iodin methods, and 0.50 per cent less thiosulphate sulphur was found by the zinc chlorid than by the iodin methods.

The following table shows the average of all results by both methods:

MONOSULPHUR EQUIVALENT	THIOSULPHATE SULPHUR		SULPHATE SULPHUR		LIME (CaO)	
	Iodin	Zinc chlorid	Iodin	Zinc chlorid	Determined	Calculated
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
5.02	1.50	1.00	0.22	0.04	9.98	10.48

When I found that there was only 9.98 per cent of lime in this sample I knew it could not be a straight lime sulphur. The iodin titrations were repeated and found to agree perfectly with those first made. Now the question arose as to what metal was reacting with the iodin; 2.5 grams were made to 100 cc. and the thiosulphate sulphur determined by the zinc chlorid method and 1.48 per cent of thiosulphate sulphur found, so that there was approximately 1.50 per cent of thiosulphate sulphur in the solution.

A determination of alkalies was made and a pure sodium salt to the extent of 1.06 per cent of sodium chlorid was found in the solution. It was thought best to test the solution for chlorids, which was done, but only a very small amount, equivalent to 0.03 per cent of sodium chlorid was found, so that it was evident that it was a sodium salt reacting with the iodin and that it was the thiosulphate was very probable from other circumstances. The sodium in the sodium chlorid was calculated to sulphur in thiosulphate and found to be equivalent to 0.56 per cent of sulphur, which left 0.94 per cent of sulphur in the form of calcium thiosulphate. Using this value for the thiosulphate sulphur instead of 1.50 per cent, the calculated lime is 9.99 per cent.

It seems to the referee, in view of these facts, that it might be said with just as much propriety that a volumetric determination and a gravimetric determination of lime will not check as to say that the calculated lime and determined lime will not check in a straight lime-sulphur solution.

WATER-SOLUBLE ARSENIC IN LEAD ARSENATE.

In regard to the recommendation relative to the time and temperature of digestion for water-soluble arsenic in lead arsenate, the referee, after consultation with the associate referee decided that the recommendations as made in this report would meet the approval of all concerned. It is to be noted that the methods of analysis are not in question at all. The time of digestion is pretty well established and a few degrees in temperature is not very material in view of the fact that both time of digestion and temperature are entirely arbitrary.

The referee is well aware and has pointed out the fact that what we are determining and calling soluble arsenic is largely soluble lead arsenate, but as both time and temperature of digestion are not absolute factors, it is probably a matter of small moment.

RECOMMENDATIONS.

It is recommended—

(1) That the method for total sulphur in lime-sulphur solutions as given in Bureau of Chemistry Circular 108, page 2 (a) be changed in the fifth line (p. 3, line 2) to read "2 grams of sodium peroxid," and as changed, be made an official method.

Hydrogen peroxid may be used as the oxidizing agent as follows: Add to the aliquot of solution 3 cc. of saturated solution (1 : 1) sodium hydroxid followed by 50 cc. of hydrogen peroxid and let stand on steam or water bath one-half hour, then acidify with hydrochloric acid and complete the determination as usual. (In case hydrogen peroxid and sodium hydrate are used, a blank must be run for the sulphur contained in them.)

(2) That the method for thiosulphate sulphur given in Bureau of Chemistry Circular 108, page 3 (b) be made an official method, the following note to be added: "In the case of a concentrate twentieth-normal iodin, instead of tenth-normal, may be used to advantage, and the exact end point for the monosulphur equivalent then determined as follows: Near the appearance of the yellow color take up a drop on a small glass rod and apply to a few drops of nickel sulphate solution on a porcelain plate."

(3) That the method for sulphate and sulphite sulphur as given in Bureau of Chemistry Circular 108, page 3 (c), be made an official method.

(4) That the method for sulphid sulphur as given in Bureau of Chemistry Circular 108, page 3 (d), have the following words in the third line, "and dissolve the sulphur in 15 cc. (1: 3) sodium hydrate," replaced with the following words: "flask with about 5 cc. of water and add 15 cc. (1:3) sodium hydroxid;" and in the fifth line strike out "1 to $1\frac{1}{2}$ hours" and replace it with "$\frac{1}{2}$ to 1 hour," and as thus changed be made an official method.

(5) That the method for total lime (CaO) in solution as given in Bureau of Chemistry Circular 108, page 3 (e), have the last line continued as follows: "or determine volumetrically with tenth-normal potassium permanganate," and as thus changed be made an official method. The sulphur may be precipitated with hydrochloric acid, the solution boiled or heated on water or steam bath until the hydrogen sulphid is driven off, the sulphur filtered off and washed, and the lime determined in the filtrate as above.

(6) That the following method of digestion for water-soluble arsenic in lead arsenate be made a provisional method, and that the present provisional method of digestion be dropped:

Water-soluble arsenic.—Weigh to 0.01 gram about 4 grams of paste; place in a tightly-stoppered flask or bottle with 250 cc. of freshly-boiled and cooled distilled water per gram and keep at 32°C. for 24 hours, shaking

well every hour during the working day (8 times in all), filtering at the end of 24 hours. Use 250 cc. of the clear filtrate for the determination; add 0.5 cc. of sulphuric acid and proceed as directed under water-soluble arsenic oxid, Bulletin 107, Revised, page 240. It is important that the solution shall be perfectly clear and the titrations carefully made. Make corrections for iodin necessary to produce the same color, using same chemicals and volumes.

(7) That the method by C. C. Hedges of Cornell University (*J. Ind. Eng. Chem.*, 1909, **1**: 208), for the determination of arsenious oxid in Paris green and other insecticides, be compared by the next referee with the official method now in use.

(8) That the Lloyd method for nicotin in tobacco and tobacco extracts be compared with the official method (Kisslings).

Lloyd method.—Weigh into a strong 200 cc. beaker 4 to 5 grams of a 3 to 7 per cent extract or 0.3 to 1 gram of a 40 per cent extract, add 2 to 3 cc. of water and sufficient ferric hydroxid mixture (equal weights ferric hydroxid and sodium acid carbonate) both ammonia-free, to make a thick paste; add 12 cc. of petrolic ether or washed gasoline, stir the whole with any convenient instrument for 2 or 3 minutes, allow to settle, and decant the solution into a separatory funnel. Repeat the extraction 4 or 5 times, decreasing the amount of ether 1 cc. each time. To the contents of the separatory funnel add 25 cc. of tenth-normal sulphuric acid and 25 cc. of water; shake the whole strongly and allow to settle. Draw off the acid solution into a deep porcelain dish, wash the contents of the funnel once or twice with 25 cc. of water and add the washings to the dish, the contents of which is titrated with tenth-normal sodium hydroxid, using neutral litmus or cochineal as indicator. 1 cc N/10 H_2SO_4=0.0162 nicotin.

A COMPARISON OF THE IODIN TITRATION AND ZINC CHLORID METHODS FOR THE ANALYSIS OF LIME-SULPHUR SOLUTIONS.

By R. C. Roark, *Associate Referee.*

For the determination of the various forms of sulphur and lime in lime-sulphur solutions, different methods have been proposed, of which two, namely, the iodin titration method as worked out by the Michigan Agricultural Experiment Station,[1] and by the referee on insecticides,[2] and the zinc chlorid method of Sutton[3] as modified by Haywood[4] and by McDonnell[5] are now before this association for consideration.

[1] Mich. Agr. Exper. Sta. Tech. Bul. 6.
[2] Bur. Chem. Bul. 162, pp. 29–30.
[3] *Volumetric Analysis*, 10th ed., pp. 342–345.
[4] *J. Amer. Chem. Soc.*, 1905, **27**: 244.
[5] Bur. Chem. Bul. 152, p. 70; Bul. 162, p. 49.

The two methods briefly are as follows: In the iodin titration method, a portion of the solution suitably diluted is titrated with standard iodin solution, the first reaction being, theoretically,

$$CaS_x + I_2 = CaI_2 + S_x.$$

This titration determines the monosulphur equivalent, and from this value the amount of lime combined with sulphur as polysulphids may be calculated. This titration does not determine the sulphur present in the solution as sulphid or as polysulphid; it is really a titration of the lime combined as calcium polysulphid. After the end point of this titration is reached, which is determined by the disappearance of the yellow color of the polysulphids, the titration is continued until the solution turns yellow from excess of iodin. By this second titration the thiosulphate sulphur is determined according to the reaction:

$$2CaS_2O_3 + I_2 = CaI_2 + CaS_4O_6,$$

the iodin acting as its own indicator. Sulphid sulphur is determined by filtering off the sulphur precipitated by the first iodin titration, oxidizing it to sulphate with sodium peroxid and determining as barium sulphate in the usual way. Sulphate and sulphite sulphur (which has been oxidized to sulphate sulphur by the iodin) are determined in the filtrate by precipitation with barium chlorid. Lime is determined on a separate aliquot of the solution, the sulphur being oxidized to sulphate by sodium peroxid and lime being precipitated from the solution of calcium sulphate by ammonium oxalate in the usual way.

In the zinc chlorid method, thiosulphate sulphur is determined by precipitating sulphids with an ammoniacal solution of zinc chlorid, filtering, neutralizing the filtrate with hydrochloric acid and titrating with standard iodin solution with starch as an indicator. Sulphid sulphur is determined by precipitating as above; the precipitate of zinc sulphid is then washed, oxidized to sulphate by means of sodium or hydrogen peroxid, and the sulphur weighed as barium sulphate. Sulphate sulphur is determined in the filtrate from the thiosulphate titration by precipitation with barium chlorid. (Sulphite sulphur, if present in the original solution, is oxidized to sulphate by the iodin solution and would, therefore, affect both the thiosulphate and sulphate determinations. If it is present at all, however, it is only in traces and may be ignored.) Lime is determined by treating a portion of the solution with hydrochloric acid, filtering from sulphur and precipitating with ammonium oxalate from the solution of its chlorid.

It will be noticed that with the iodin titration method, all the determinations with the exception of lime are made on the same aliquot, whereas with the zinc chlorid method, every determination is made on a separate

aliquot with the exception of thiosulphate and sulphate sulphur. The determination of total sulphur according to the two methods differs only in the use of the oxidizing agent, which is sodium peroxid in the iodin titration method and hydrogen peroxid in the zinc chlorid method.[1] Both give accurate results and so are not discussed in this paper.

OBJECTIONS TO THE IODIN TITRATION METHOD.

Assuming in the iodin titration method that the forms of sulphur present include only the polysulphid, the thiosulphate, the sulphite, and the sulphate of calcium (an assumption that later we shall show to be incorrect) the method is open to the following objections:

(1) In the titration for the monosulphur equivalent and thiosulphate sulphur, dilution of the aliquot being titrated has a marked effect on the results, as has been pointed out by McDonnell (See Bur. Chem. Bul. 162, p. 40).

The present referee has found that dilution has an effect on titration as shown in a letter to C. C. McDonnell under date of February 21, 1913:

> I found that when the dilution amounted to 100 cc. it was necessary to titrate rapidly and use an external indicator for the first end point and starch solution for the other. With dilutions of 150 to 200 cc. I found that the decomposition began so quickly and was so rapid that any values might be obtained, depending upon the rate of titration.

It has been urged that such high dilutions were not contemplated by the method, but a dilution of a 10 cc. aliquot to 60 cc. or to 100 cc. can not be considered an excessive dilution, yet in one case a dilution from 20 cc. to 60 cc. decreased the monosulphur equivalent from 6.00 to 5.94 and increased the percentage of thiosulphate sulphur from 1.73 to 2.00; in another case a dilution from 50 cc. to 100 cc. decreased the monosulphur equivalent from 4.59 to 4.40 and increased the thiosulphate sulphur from 1.34 to 1.75.

(2) In the second place, the end point of either of these titrations can not, at the best, be determined closer than 0.10 cc. of tenth-normal iodin solution each, which on an aliquot representing 0.25 gram of sample (5 grams to 200 cc., a dilution recommended by the referee for concentrates), would cause an error of 0.07 for the monosulphur equivalent value and an error of 0.28 per cent for the thiosulphate sulphur value. It may be that these errors are compensating, but no method is to be considered accurate that depends on an uncertain compensation of errors.

Unless the end point of the monosulphur equivalent titration be determined by means of nickel sulphate as an outside indicator, an error of more than 0.10 cc. of tenth-normal iodin may easily be made. If an outside indicator is used, the withdrawal of portions of the solution (more

[1] Avery, Bur. Chem. Bul. 90, p. 105.

especially when it is of small volume as it must be to avoid the effect of dilution) introduces an error in the titration for thiosulphate sulphur and also in the determination of sulphid sulphur, as particles of suspended sulphur are removed with the solution when a portion is withdrawn for testing.

Furthermore, the titration of thiosulphate sulphur with iodin as its own indicator, especially in the presence of precipitated sulphur, can not be as accurate as where starch paste is used to show the end point. But if starch paste is used, it interferes with the filtration of the precipitated sulphur so that this is another instance of what occurs throughout the iodin titration method, that is, the use of a less accurate method for one determination so that the succeeding determination made on the same aliquot will not be spoiled.

That the end points of these iodin titrations are difficult of determination is shown by the results of the different analysts coöperating with the referee in 1912 (See Bur. Chem. Bul. 162, pp. 33–34). These results varied so that out of fourteen values for thiosulphate sulphur, the referee discarded seven, or one-half. Results for monosulphur equivalent on sample No. 2 by two analysts were also thrown out.

(3) In the determination of sulphid sulphur by the iodin titration method, the sulphur precipitated by the iodin titration is filtered off, oxidized with sodium peroxid, and precipitated as barium sulphate. This sulphur can not be filtered at once as it will pass through the finest filter paper. It has been found necessary to allow the sulphur to stand for several hours, or overnight, before filtering, thus causing a delay in the completion of the analysis—a delay that is not met with in the zinc chlorid method where the precipitate of zinc sulphid can be filtered immediately.

The filtration of sulphur at best is an unsatisfactory process and the chances of error through manipulation as compared to the filtration of zinc sulphid, are relatively as 3 to 1, which is the ratio of the molecular weight of zinc sulphid to the atomic weight of sulphur.

(4) Results for sulphate sulphur are higher by the iodin titration than by the zinc chlorid method, as is shown in the following table:

SAMPLE	METHOD	
	Iodin titration	Zinc chlorid
1913 A. O. A. C. No. 1	0.07	0.03
	0.09	0.02
1913 A. O. A. C. No. 2	0.11	0.05
	0.10	0.06
Misc. No. 13826	0.16	0.03
	0.16	0.03
Misc. No. 14799	0.22	0.04
	0.21	0.03

As an explanation of this, it would seem probable that in the iodin titration some of the sulphur other than sulphite sulphur is oxidized to sulphate. It is not unreasonable to suppose that such a strong oxidizing agent as iodin does oxidize some of the sulphur compounds present to sulphate.

(5) For the determination of lime, the referee recommends using an aliquot which will give in the case of a concentrate containing approximately 10 per cent calcium oxid, only 0.025 gram of ignited lime. It is maintained by the writer that for accurate results a sufficiently large aliquot should be taken to give at least 0.100 gram of ignited lime. No objection, theoretical or otherwise, can be brought against this.

OBJECTIONS TO THE ZINC CHLORID METHOD.

(1) It has been objected that in the precipitation of sulphids by the ammoniacal zinc chlorid solution, the zinc sulphid precipitate may carry down and hold some of the thiosulphate, thus making the results for sulphid sulphur high and the results for thiosulphate sulphur low.

Both calcium and zinc thiosulphates are extremely soluble in water and are stable unless the solution is boiled, whch is not done in this method, so there is no reason for their not appearing in the filtrate from the zinc sulphid precipitate due to insolubility or to decomposition. Moreover, McDonnell[1] has found that on adding thiosulphate sulphur as sodium thiosulphate to lime sulphur solutions, up to 50 times the amount occurring in the sample, the whole amount added could be recovered when determined according to this method. This proves that no thiosulphate sulphur is destroyed or held up by the zinc sulphid precipitate. Further proof of this statement is to be found in the results of the analysts on the 1911 lime-sulphur samples.[2] Sample No. 2 was the same as No. 1, except for the addition of 2.02 per cent of thiosulphate sulphur as sodium thiosulphate. The average difference in thiosulphate sulphur in these two samples from 19 determinations is 1.98 per cent, which agrees closely with the theoretical 2.02 per cent.

(2) As regards tediousness, zinc sulphid may be filtered at once and with accuracy, whereas in the iodin titration method the precipitated sulphur must stand sometime before being filtered, and then with the probability of losing appreciable quantities.

RÉSUMÉ OF OBJECTIONS.

To sum up the criticisms of the probable errors in the two methods due to manipulation.

[1] Bur. Chem. Bul. 162, p. 41.
[2] Bur. Chem. Bul. 152, p. 71.

(1) In the titration of thiosulphate sulphur by the iodin titration method, it is shown that errors may arise, (a) from reading the end point of the monosulphur equivalent titration more especially when nickel sulphate is not used as an outside indicator and any error in this titration causes a considerable error in the titration for thiosulphate sulphur which follows (1 cc. N/10 I = 0.0016 gram of sulphid sulphur, but = 0.0064 gram of thiosulphate sulphur): (b) from reading the end point of the thiosulphate titration where starch is not used as an indicator; (c) from the effect of even moderate dilution of the aliquot which decreases the values for monosulphur equivalent and increases those for thiosulphate sulphur.

In the zinc chlorid method only one iodin titration is made in determining thiosulphate sulphur and starch is used as an indicator, conditions more favorable to accuracy than are those of the iodin titration method.

(2) That in the determination of sulphid sulphur, zinc sulphid may be filtered at once, whereas sulphur precipitated by iodin must stand for several hours before filtering, and even then with the chance of loss by running through the paper. Moreover, zinc sulphid may be washed free of thiosulphate, whereas it is yet to be shown that in filtering precipitated sulphur which has stood in a solution containing sulphur compounds, that the sulphur particles do not hold some of these sulphur compounds.

(3) In the zinc chlorid method, sulphate sulphur is determined in the filtrate from the thiosulphate sulphur titration where only a few cubic centimeters of iodin have been used, whereas in the iodin titration method sulphate sulphur is determined after the solution containing unstable and easily oxidizable sulphur compounds has been exposed to the action of a large amount of iodin, conditions favorable to the oxidation of sulphur, in forms additional to sulphite, to sulphate.

(4) According to the method of the referee, lime is precipitated from a solution in which it is present as sulphate, whereas according to the method of the associate referee, it is precipitated from a solution of the chlorid and an aliquot is used which gives about four times as much ignited lime as will be obtained according to the referee's method.

COMPOSITION OF LIME-SULPHUR SOLUTIONS.

In discussing the relative merits of the iodin titration and of the zinc chlorid methods for the analysis of lime-sulphur solutions, it has been assumed that the only calcium sulphur compounds present were polysulphids, thiosulphate, and small amounts of sulphite and sulphate. On carefully looking up the literature, however, it is found that such is undoubtedly not the case.

Review briefly what compounds have been shown to be present in pure lime-sulphur solutions, and what effect these compounds, other than those already mentioned, would have on the determinations as made according

to the two methods. Beginning with the sulphids, the simplest is calcium monosulphid (CaS), which can not exist in solution, however, as it is decomposed by water as follows:

$$2CaS+2H_2O=Ca(SH)_2+Ca(OH)_2$$ [1]

The next in series is calcium bisulphid (CaS_2). Tartar and Bradley[2] obtained a compound whose composition corresponded very closely to this formula by evaporating lime-sulphur solution in an atmosphere of hydrogen over sulphuric acid in the dark and at a low temperature, washing the residue with carbon disulphid until all free sulphur was extracted and drying in a current of hydrogen.

While calcium trisulphid (CaS_3) has not been isolated from a lime-sulphur solution, it seems probable that it would be formed by the boiling together of lime and sulphur. The very recent work of Tartar[3] shows that potassium trisulphid (K_2S_3) is formed in the primary reaction of sulphur with potassium hydroxid in heated aqueous solution, and from analogy, calcium trisulphid should be formed in the preparation of a lime-sulphur solution.

Calcium tetrasulphid (CaS_4) is formed by boiling together 1 equivalent of calcium monosulphid with 3 equivalents of sulphur,[4] or by the action of sulphur on lime in heated aqueous solution.[5]

Calcium pentasulphid (CaS_5) may be formed by dissolving sulphur in a solution of calcium hydrosulphid,[6] by boiling calcium monosulphid with sulphur,[7] or by boiling sulphur with lime.[8] No higher sulphid of calcium than the pentasulphid is known to exist.

In this connection it may be well to recall that the principal objection brought against the zinc chlorid method last year by the present referee was that, according to analyses by this method a sulphid of calcium higher than the pentasulphid was shown to exist. This claim was based on the results on the two association samples for 1911, in which ratios of 5.3 to 1 and 5.6 to 1 were found for sulphid sulphur and lime.[9] These ratios, however, were obtained by dividing the values for sulphid sulphur, determined according to the zinc chlorid method, by the values for monosulphur equivalent determined by the iodin titration method. A slight error in this latter value (which could have been made from the effect of dilution alone, as the determination was made before the work of Mc-

[1] Abegg's *Handbuch der anorg. chemie*, 1905, **2** (2): 116.
[2] *J. Ind. Eng. Chem.*, 1910, **2**: 275.
[3] *J. Amer. Chem. Soc.* 1913, **35**: 1746.
[4] Schöne, *Pogg. Ann.*, 1862, **117**: 75.
[5] Tartar and Bradley, loc. cit., p. 274.
[6] Divers and Schimidzu, *J. Chem. Soc.*, 1884, **45**: 284.
[7] Gmelin-Kraut, *Handbuch der anorg. chemie*, 1909, **2** (2): 222.
[8] Tartar and Bradley, loc. cit., p. 277.
[9] Letter to C. C. McDonnell under date of November 17, 1911.

Donnell showing the marked effect of dilution had been brought to the attention of the referee) would change the ratios materially.

On association sample No. 1 for 1911 the present referee obtained a value for lime (CaO) of 6.05 per cent, agreeing well with the value calculated from his results by the iodin titration method, namely, 6.04 per cent. According to the closely agreeing analyses by one of the Bureau of Chemistry chemists, however, the lime in this sample was only 5.53 per cent, or 0.52 per cent less than found by the present referee. From this it is seen that the original objection of the present referee to the zinc chlorid method was based on faulty premises.

McDonnell[1] showed that among the results of analyses of 29 lime-sulphur solutions tabulated in Michigan Technical Bulletin No. 6, there were 5 having ratios of total sulphid sulphur to monosulphur equivalent greater than 5 to 1, the highest being 5.11 to 1. On the other hand, from the analyses of 33 samples of lime-sulphur solutions examined by the zinc chlorid method, only 1 showed a ratio of polysulphid sulphur to lime greater than 5 to 1, namely 5.08 to 1.

The work that was done by Van Slyke[2] in showing that no sulphid higher than the penta is present in lime-sulphur solution, was done according to the zinc chlorid method, and if this method does not give correct results, this very conclusion would be erroneous.

In addition to the sulphids of calcium, there are in a lime-sulphur solution certain oxy-sulphur compounds, of which calcium thiosulphate is found in largest amount. First prepared by Herschell[3] in 1819, it is formed whenever lime and sulphur are brought together in heated aqueous solution, the amount formed being dependent on concentration and length of boiling.[4] Calcium sulphite ($CaSO_3$) exists in small amount in lime-sulphur solution as shown by Van Slyke.[5]

Calcium sulphate ($CaSO_4$) exists in traces only in lime-sulphur solution.[6]

Hydrogen sulphid is present in small amount in nearly all commercial concentrated lime-sulphur solutions. In the preparation of lime-sulphur solution, hydrogen sulphid is given off in large quantities,[7] so that it is natural to expect its presence in the finished product. Furthermore, on dilution of a lime-sulphur solution some hydrogen sulphid is produced according to the reaction:

$$CaS_x+2H_2O=Ca(OH)_2+H_2S+S_{x-1}.$$

[1] Bur. of Chem. Bul. 162, p. 38.
[2] N. Y. Agr. Exper. Sta. (Geneva) Bul. 319, p. 394.
[3] *Edinburgh Phil. J.*, 1819, **1**: 8.
[4] Fordos and Gelis, *Annales de Chimie et de Physique* 1846, (3) **18**: 86; Senderens, Bul. de la Société Chimique de Paris, 1891 (3) **6**: 800; Tartar and Bradley, loc. cit.
[5] N. Y. Agr. Exper. Sta. (Geneva) Bul. 319, p. 383.
[6] Van Slyke, loc. cit., pp. 383 and 396.
[7] Herschell, Fordos and Gelis, Senderens, Schöne, loc. cit., and Firard, *Compt. Rend.*, 1863, **56**: 797.

In addition to these well-known compounds, there are others which are formed by the interaction of these, or by the action of water and oxygen. There is some hydrosulphid formed by the action of hydrogen sulphid with lime:

$$Ca(OH)_2+2H_2S=Ca(SH)_2+2H_2O^1$$

Also, hydrosulphid is formed as an intermediate product in the reaction between polysulphid and water:

$$2CaS_x+2H_2O=Ca(SH)_2+Ca(OH)_2+2S_{x-1}.$$

The presence of hydrosulphid in lime-sulphur solution has been disputed, and in support of this contention the work of Tartar and Bradley is often cited. A careful reading of their article, however, shows that they do not make the statement that no hydrosulphid is present. They state: "Our tests show the absence of appreciable quantities of hydrosulphid."[2] This conclusion is based on the results of one quantitative experiment.[3] They determined sulphid sulphur by titration with standard ammoniacal zinc chlorid solution and also by determining the hydrogen sulphid evolved upon addition of dilute acid. By the first method, only one-half the sulphur combined as hydrosulphid would be shown, as it would be precipitated as zinc hydrosulphid, but calculated as zinc sulphid (ZnS); all the sulphid sulphur would be evolved as hydrogen sulphid upon addition of acid. In this way they found in a solution 3.42 grams of sulphur per 100 cc. by the sulphid sulphur method and 3.44 grams of sulphur per 100 cc. by the hydrogen sulphid method, or 0.020 gram more.

Sulphur present as hydrosulphid would be twice 0.020 gram =0.040 gram, or 1.13 per cent of the total sulphid sulphur present, surely more than a trace. Moreover, on dilution, a condition which prevails in the course of analysis, another oxysulphur compound is formed, namely, hydroxyhydrosulphid:

$$Ca(SH)_2+H_2O=Ca(SH)(OH)+H_2S$$

It is doubtful if more than a trace of this compound exists at any one time, but as these reactions are reversible it is formed as an intermediate product, (1) in the reaction between lime and hydrogen sulphid, and (2) in the decomposition of polysulphids by water.

Consider what effect these hydrosulphur compounds would have on the iodin titration method. Hydrogen sulphid would be titrated as monosulphur equivalent, making the results for that high, and, of course, the value of lime calculated from it high. Calcium hydrosulphid dissolves in water,

[1] Divers and Schimidzu, *J. Chem. Soc.*, 1884, **45**: 271.
[2] Loc. cit. p. 277.
[3] Loc. cit. p. 274.

forming a colorless solution, hence by the iodin titration method it could escape titration with the polysulphids and be determined with, and calculated as, thiosulphate sulphur, which, as results show, is higher by the iodin titration than by the zinc chlorid method. The existence of a hydrosulphid is also indicated by the fact that in the monosulphur equivalent titration the end point is always reached quicker when taken by the disappearance of the yellow color than when nickel sulphate is used as an outside indicator.

By the zinc chlorid method any hydrosulphid or any hydroxyhydrosulphid present would be precipitated as zinc sulphid and would not appear, nor be titrated, in the filtrate as thiosulphate sulphur.

Certain other oxysulphur compounds of calcium are known. Herschell[1] by boiling together for one hour, sulphur and lime in 20 parts of water, obtained orange-colored crystals which, after drying over sulphuric acid in a vacuum showed upon analysis the composition $Ca_2S_2O_2{\cdot}4H_2O$. As later determined by Schöne[2] the formula is $Ca_4S_4O_3{\cdot}12H_2O$, or, according to the analysis of Geuther[3] $Ca_3S_3O_2$ with either 10 or 11 molecules of water. In addition to this compound, which is known as Herschell's crystals, there is another calcium sulphur complex which has been found in lime-sulphur solution, namely, Büchner's crystals, whose composition is represented by the formula $Ca_4S_4O_4{\cdot}18H_2O$[4] or by $Ca_3S_3O_3{\cdot}14$ or $15H_2O$.[5]

Tartar and Bradley, in preparing pure lime-sulphur solutions, observed the formation of orange-red needle-shaped crystals which they stated "were undoubtedly the oxysulphids of calcium."[6]

That these crystals occurred in solutions such as might be met with at any time is shown by the analysis. One solution contained 5 grams of lime (CaO) and 10.5 grams of total sulphur; the other 9.45 grams of lime (CaO) and 20 grams of total sulphur per 100 cc. If these oxysulphids compounds exist in solutions such as these in so large amount as to crystallize out on cooling, may we not expect them in appreciable quantities in most every lime-sulphur solution? While not more than a trace of free calcium hydroxid ($Ca(OH)_2$) may be present in a freshly-prepared lime-sulphur solution,[7] it is formed in appreciable amounts upon dilution according to the reaction.

$$CaS_5+2H_2O=Ca(OH)_2+H_2S+4S$$

and would be present, therefore, in lime-sulphur solutions which had stood for some time and become partially decomposed.

[1] *Edinburgh Phil., J.*, 1819, **1**: 8.
[2] *Pogg. Ann.*, 1862, **117**: 78.
[3] *Ann. Chem. (Leibig)*, 1884, **224**: 190.
[4] Schöne, loc. cit., p. 85.
[5] Geuther, loc. cit., p. 193.
[6] *J. Ind. Eng. Chem.*, 1910, **2**: p. 273.
[7] Tartar and Bradley, loc. cit., p. 273.

As pointed out by McDonnell,[1] there is no reason why calcium hydroxid can not be added to a lime-sulphur solution after its preparation and marketed in such form. McDonnell showed that by adding 15 cc. of clear lime water to a lime-sulphur solution having a monosulphur equivalent of 5.26 and 3.54 per cent of thiosulphur, the value for monosulphur equivalent was increased to 6.54 and thiosulphate to 4.12 per cent.

Undoubtedly the lime in the complex oxysulphid compounds previously mentioned is loosely combined and on titration of the solution with iodin would consume it, and, hence, add to the values for thiosulphate.

SUMMARY.

In addition to the tetra and pentasulphid, the thiosulphate and the sulphite and sulphate of calcium, admitted by the referee to be present in a concentrated lime-sulphur solution, there are some calcium bisulphid, very probably some calcium trisulphid, undoubtedly small amounts of hydrogen sulphid and calcium hydrosulphid, traces of free calcium hydroxid, and appreciable amounts of oxysulphid compounds of variable composition. On dilution for analysis, there will be formed more hydrosulphid and more free calcium hydroxid, together with small amounts of calcium hydroxyhydrosulphid. The referee claims that the accuracy of the iodin titration method is proved in that the lime (CaO) in solution calculated from the values for monosulphur equivalent, thiosulphate and sulphate sulphur agrees with the lime determination. If, as the referee assumes, the solution contained only polysulphids, thiosulphate, sulphite and sulphate of calcium, this would be true and the two values for lime should agree. As we have just shown, however, a lime-sulphur solution contains in addition to these compounds small amounts of hydrogen sulphid and calcium hydrosulphid, calcium bisulphid, calcium trisulphid, traces of free calcium hydroxid and appreciable quantities of complex oxysulphid compounds; therefore, even if the iodin titrations gave absolutely correct results for monosulphur equivalent and thiosulphate sulphur (which is never true, owing to the effect of dilution, error in reading end points, etc.) lime (CaO) could not be calculated because of the presence of these other sulphur compounds of calcium.

The results of analysis of some commercial concentrated lime-sulphur solutions bear out what should be expected from this theory. Lime was determined according to the method recommended by the author, in which the calcium is precipitated from a solution of its chlorid, using a sufficiently large aliquot to give an accurately weighable ignited precipitate. Sulphate sulphur was determined according to the zinc chlorid

[1] Bur. Chem. Bul. 162, p. 41.

method. If determined according to the iodin titration method the results would have been higher, thus making the results for calculated lime still further from those of determined lime.

Thiosulphate sulphur and monosulphur equivalent were determined by the iodin titration method, nickel sulphate being used as an outside indicator for the first titration and the end point of the second titration being checked always by adding a little starch paste. Ten cubic centimeter aliquots, representing about 0.4 gram of concentrated solution, were diluted to 35 cc. only before titration to avoid the effect of dilution. The results given are the mean of closely-agreeing determinations.

Analyses of concentrated lime sulphur solutions.

LABORATORY NO.	ZINC CHLORID METHOD				IODIN TITRATION METHOD		LIME (CaO)		
	Total sulphur	Sulphid sulphur	Sulphate sulphur	Thio-sulphate sulphur	Thio-sulphate sulphur	Monosul-phur equiva-lent	Deter-mined	Calcu-lated	Differ-ence
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
13826	25.00	24.24	0.03	0.87	1.44	5.00	9.75	10.05	−0.30
14156	25.63	24.72	0.04	0.76	1.62	5.08	10.02	10.37	−0.35
14799	24.51	23.47	0.04	0.81	1.51	5.09	9.96	10.29	−0.33
14883	24.10	22.78	0.07	0.94	1.30	4.69	9.25	9.44	−0.19
14994	25.17	24.25	0.05	0.92	2.26	4.68	10.17	10.24	−0.07
15156	25.24	24.01	0.04	1.09	1.99	4.90	10.09	10.38	−0.29
15157	26.08	25.53	0.03	0.60	1.65	5.20	10.18	10.58	−0.40
15819	24.88	23.80	0.03	0.87	1.70	4.92	9.78	10.14	−0.36
15825	21.85	20.92	0.04	1.10	2.00	4.50	9.01	9.68	−0.67
15874	24.99	24.34	0.04	0.65	1.83	4.76	9.77	9.99	−0.22
16043	24.60	23.64	0.04	1.00	1.83	4.78	9.68	10.02	−0.34
16140	21.78	20.14	0.03	1.52	2.39	4.13	9.09	9.36	−0.27
16143	22.51	21.16	0.03	1.46	2.34	4.38	9.19	9.75	−0.56
16146	22.97	22.14	0.04	0.88	1.59	4. 6	9.16	9.26	−0.10
16235	25.38	24.29	0.03	0.90	1.37	5.18	10.09	10.30	−0.21
16244	24.73	23.82	0.03	0.72	1.42	4.99	9.77	10.03	−0.26
16397	24.85	24.23	0.04	0.72	1.65	4.99	9.75	10.25	−0.50

In every case it is seen that the value for lime calculated from results obtained by the iodin titration method is higher than that determined gravimetrically, the difference ranging from 0.07 to 0.67 per cent with an average of 0.32 per cent. An explanation of this will be given later.

In addition to these, the results of other workers show that the calculated and determined values for lime do not agree. The following table gives the values for lime as determined by Tartar and Bradley[1] in the lime-sulphur solutions studied by them. The values for calculated lime have been figured from their results for sulphite and sulphate sulphur, thiosulphate and "sulphid" sulphur, which they determined by titration with zinc chlorid solution:

[1] *J. Ind. Eng. Chem.*, 1910, **2**: 273, 275, 276.

Results by Tartar and Bradley.

DESCRIPTION OF SAMPLE	GRAMS PER 100 CC. LIME		
	Determined	Calculated	Difference
Commercial	12.12	11.77	+0.35
Commercial	12.86	14.07	−1.21
Commercial	12.38	12.73	−0.35
55 grams of lime + 110 grams of sulphur + 400 cc. water boiled 1½ hours	9.49	9.47	+0.02
55 grams of lime + 55 grams of sulphur + 450 cc. water boiled 1 hour	4.99	5.27	−0.22
60 grams of lime + 110 grams of sulphur + 450 cc. water boiled 1 hour	9.45	9.65	−0.20
55 grams of lime + 110 grams of sulphur + 450 cc. water boiled 1 hour	9.68	9.69	−0.01
60 grams of lime + 110 grams of sulphur + 450 cc. water boiled 2½ hours	8.24	8.50	−0.26
55 grams of lime + 55 grams of sulphur + 450 cc. water boiled 1 hour	5.15	5.34	−0.19
55 grams of lime + 55 grams of sulphur + 450 cc. water boiled 2½ hours	5.10	5.32	−0.22
60 grams of lime + 110 grams of sulphur + 450 cc. water boiled 1 hour	9.45	9.65	−0.20
60 grams of lime + 110 grams of sulphur + 450 cc. water boiled 2½ hours	8.39	8.49	−0.10

Assuming that titration with zinc chlorid solution yields the same results for monosulphur equivalent, or "sulphid" sulphur, as it is termed by Tartar and Bradley, as when iodin solution is used (an assumption held to be true by Harris and by Averitt), and assuming further, according to the contention of the referee, that only the polysulphid, the thiosulphate, the sulphite and sulphate of calcium are present, it is seen from the above results that the zinc chlorid method gives, if anything, high results for thiosulphate sulphur. From all the work that has been done on the comparison of the two methods, however, thiosulphate sulphur by the iodin titration method is invariably higher than thiosulphate sulphur by the zinc chlorid method and so must necessarily be farther from the true figures.

The official samples of lime-sulphur solution sent out this year, according to the analyses of the Bureau chemists, do not show agreement between the calculated and determined values for lime:

SAMPLE AND ANALYST	LIME		
	Determined	Calculated	Difference
	per cent	*per cent*	*per cent*
Sample 1			
Analyst 1	2.24	2.56	−0.32
Analyst 2	2.23	2.53	−0.30
Sample 2			
Analyst 1	4.66	4.99	−0.33
Analyst 2	4.65	4.95	−0.30

The present referee himself,' from the analysis of two commercial concentrated lime-sulphur solutions as received from the manufacturers, found that lime determined did not agree with lime calculated:

Analysis by Averitt.

SAMPLE	LIME		
	Determined	Calculated	Difference
	per cent	*per cent*	*per cent*
"A" (Misc. No. 14799)....	9.99	10.49	−0.50
"B" (Misc. No. 13826)....	[1]9.76	10.12	−0.36

[1] The mean of ten closely-agreeing results by 3 analysts determined according to both the Bureau of Chemistry and the referee's methods.

In Sample "A" nine closely-agreeing results by the same analysts gave a mean of 9.97 per cent.

The analyses presented in Michigan Technical Bulletin No. 6 do not bear out the contention of the author of the iodin titration method that lime may be accurately computed from the results for the various forms of sulphur. In the table on the following page are given the values for determined lime as they appear in the various tables in this bulletin, together with the values for calculated lime which have been figured from the values given for monosulphid sulphur, thiosulphate sulphur and sulphite and sulphate sulphur. All results have been figured to per cent by weight. It will be noticed that the differences between the two values for lime vary from −1.18 to +0.44, a variation of 1.62.

From this table it is seen that in twenty-seven out of the thirty-two samples, the difference between the calculated and determined values for lime is 0.05 per cent or more; in eighteen, the difference is 0.10 per cent or more; in fourteen the difference is 0.15 per cent or more; in nine the difference is 0.20 per cent or more; in three the difference is over 0.30 per cent, and in one the difference amounts to 1.18 per cent. Lime can be determined so that duplicates run within 0.05 per cent of each other; therefore it appears that in twenty-seven out of thirty-two cases the method of calculating lime from the results for the various forms of sulphur affords no check whatever on the true amount present.

In Table III of Michigan Technical Bulletin No. 6, out of fifteen samples, nine have differences of 0.06 or more between the calculated and determined values for lime, while five have differences of 0.10 or more.

It may be urged that the experimental errors in the determination of the different forms of sulphur may account for these discrepancies. Let us inquire more closely into this contention. Sulphate and sulphite sulphur

Results from Michigan Technical Bulletin No. 6.

SAMPLE	LIME (CaO)			REFERENCE
	Determined	Calculated	Difference	
	per cent	*per cent*	*per cent*	
4A	7.16	7.08	+0.08	Table V, p. 10.
6A	6.92	8.10	−1.18	Table V, p. 10
1A	8.02	7.84	+0.18	Table VII, p. 11
1B	9.00	8.80	+0.20	Table VII, p. 11.
2A	8.30	8.16	+0.14	Table VII, p. 11.
2B	8.44	8.43	+0.01	Table VII, p. 11.
3D	8.85	8.58	+0.27	Table VII, p. 11.
1A	7.18	7.07	+0.11	Table VIII, p. 12.
1B	7.11	7.06	+0.05	Table VIII, p. 12.
1C	7.09	7.30	−0.21	Table VIII, p. 12.
2A	6.97	6.96	+0.01	Table VIII, p. 12.
2B	6.88	6.77	+0.11	Table VIII, p. 12.
2C	7.10	7.13	−0.03	Table VIII, p. 12.
3A	9.83	9.50	+0.33	Table VIII, p. 12.
3B	8.93	8.77	+0.16	Table VIII, p. 12.
3C	9.54	9.46	+0.08	Table VIII, p. 12.
4A	8.85	8.41	+0.44	Table VIII, p. 12.
4B	8.65	8.39	+0.26	Table VIII, p. 12.
4C	8.67	8.72	−0.05	Table VIII, p. 12.
5A	7.79	7.65	+0.14	Table VIII, p. 12.
5B	7.95	7.76	+0.19	Table VIII, p. 12.
6A	8.21	8.00	+0.21	Table VIII, p. 12.
6B	8.07	8.03	+0.04	Table VIII, p. 12.
7A	5.77	5.61	+0.16	Table VIII, p. 12.
7B	5.66	5.58	+0.08	Table VIII, p. 12.
7C	5.79	5.84	−0.05	Table VIII, p. 12.
8A	6.52	6.24	+0.28	Table VIII, p. 12.
8B	6.16	6.07	+0.09	Table VIII, p. 12.
8C	6.31	6.16	+0.15	Table VIII, p. 12.
3D	8.89	8.81	+0.08	Table IX, p. 14.
4D	8.51	8.50	+0.01	Table IX, p. 14.
8D	6.20	6.29	−0.09	Table IX, p. 14.

are present only in traces and are generally determined within 0.01 per cent, which would affect the value of lime calculated therefrom $0.01 \times 1.748 = 0.017$ or 0.02. In many cases, as in sample No. 3, Table III (Mich. Tech. Bul. No. 6), there is no sulphate or sulphite sulphur present and yet in this case there is a difference of 0.13 between the calculated and determined values for lime. In general, then, the error in the determination of sulphur in the form of sulphite and sulphate can affect the calculated value for lime but little. In the determination of thiosulphate, every 0.10 cc. N/10 I = 0.00064 gram thiosulphate sulphur = 0.00056 gram CaO. Therefore, for every error of 0.10 cc. of tenth-normal iodin made in the titration for thiosulphate, the percentage of lime calculated therefrom would be affected by 0.14 per cent, assuming that 0.4 gram concentrate containing 10 per cent of lime is under titration.

But in the iodin titration method, any error in the monosulphur equivalent titration affects the thiosulphate titration. Thus, if 0.10 cc. of tenth-

normal iodin too much is used for the first titration, the second titration will be short just that much.

Now, 0.10 cc. N/10 I = 0.00016 gram sulphid sulphur = 0.00028 gram CaO. Thus, from the monosulphur equivalent titration, assuming 0.10 cc. of tenth-normal iodin too much to be used, 0.00028 gram of lime too much would be calculated, but the succeeding thiosulphate titration being 0.10 cc. short and 0.00056 gram of lime being calculated therefrom, there would be the result of running over 0.10 cc. of tenth-normal iodin in the monosulphur equivalent titration, 0.00028 gram of lime less, or 0.07 per cent less calculated lime on a 0.4 gram aliquot running 10 per cent lime. Assuming the errors to run the other way, too little monosulphur equivalent and too much thiosulphate, there would be for every 0.10 cc. of tenth-normal iodin that the monosulphur equivalent titration was short, 0.00028 gram of lime, or 0.07 per cent more calculated lime.

An error of more than 0.10 cc. of tenth-normal iodin in these titrations would be excessive provided the precautions emphasized by the associate referee, namely, small dilution, and the use of nickel sulphate and starch paste as indicators, are observed, therefore, experimental errors in the determination of the various sulphur compounds (assuming only the polysulphid, the thiosulphate, the sulphite and sulphate to be present) are insufficient to explain the large errors in the values for calculated lime figured therefrom.

The logical conclusion, therefore, is that other sulphur compounds of calcium are present. How the presence of these other bodies will affect the values for calculated lime will now be shown.

WHY THE VALUES FOR DETERMINED LIME ARE LOWER THAN THE VALUES CALCULATED FROM RESULTS BY THE IODIN TITRATION METHOD, BUT HIGHER THAN THE VALUES CALCULATED FROM RESULTS BY THE ZINC CHLORID METHOD.

Lime (CaO) in commercial concentrates calculated from results by the iodin titration method are higher, while lime calculated from results by the zinc chlorid method are lower than the determined values for lime. The explanation for this is as follows:

The complex oxysulphid compounds which have been found by several observers to be present in pure lime-sulphur solutions are generally represented by the following formulae: $2CaO \cdot CaS_3 \cdot H_2O$; $3CaO \cdot CaS_4 \cdot 12H_2O$; $4CaO \cdot CaS_4 \cdot 18H_2O$; $3CaO \cdot CaS_3 \cdot H_2O$.

In titrating a lime-sulphur solution, the iodin would react with one of these compounds as follows:

$$4CaO \cdot CaS_4 18H_2O + I_2 = CaI_2 + 4S + 4Ca(OH)_2 + 14H_2O$$

This reaction would take place while the monosulphur equivalent titration was being made. The calcium hydroxid would then react with iodin according to the equation:

$$2Ca(OH)_2+4I=Ca(OI)_2+CaI_2+2H_2O$$

This reaction between calcium hydroxid and iodin would probably take place both in the monosulphur equivalent titration and in the thiosulphate titration.[1]

According to this equation 2 I=1CaO, but according to the reaction between calcium thiosulphate and iodin, 2 I=4 thiosulphate S; and since thiosulphate S times 0.874=CaO combined with it as calcium thiosulphate, $2\ I=4\times0.874=3.5$ CaO. Therefore, for every molecule of calcium hydroxid titrated in the thiosulphate titration with iodin, 3.5 molecules will be calculated therefrom and reported according to the iodin titration method of analysis. If the free calcium hydroxid is titrated as monosulphur equivalent, for every molecule present 1.75 molecules will be calculated. Assuming that as much free calcium hydroxid is titrated as monosulphur equivalent as is titrated as thiosulphate sulphur, the following is true: For every molecule of lime but one of the complex oxysulphid compounds present in the lime sulphur solution, 2.63 molecules of lime will be calculated when the sample is analyzed according to the iodin titration method.

It is interesting to note the result on this complex oxysulphid compound when the solution is analyzed by the zinc chlorid method. On addition of the ammoniacal zinc chlorid, all the sulphur of the compound, which is present as sulphid sulphur, will be precipitated as zinc sulphid or polysulphid. It may be that the whole compound will be precipitated, but at any rate all the sulphur will be. Assuming that the free calcium hydroxid does pass into the filtrate from the zinc sulphid precipitate before titration with iodin for thiosulphate sulphur all the calcium hydroxid, together with the ammonia, will have been changed to chlorid in the neutralization with hydrochloric acid, and will not, therefore, interfere with the titration for thiosulphate sulphur according to the zinc chlorid method.

In the zinc chlorid method, this extra calcium hydroxid would not be titrated and so would not be calculated at all, but would appear in the gravimetric determination, thus making the determined value higher than the calculated. The presence of free calcium hydroxid would tend to affect results in the same manner as the complexes just mentioned. The presence of hydrogen sulphid would tend to make the results for monosulphur equivalent high and the value of lime calculated therefrom correspondingly high. The presence of hydrosulphid or hydroxyhydro-

[1] Bur. Chem. Bul. 162, p. 41.

sulphid would tend to raise the results for thiosulphate sulphur as shown by McDonnell[1] and, of course, the value of lime calculated therefrom.

From a study of the tables of results of analysis of commercial concentrated lime-sulphur solutions on page 87 it is seen that the theory of this explanation is verified in every instance by the facts.

CONCLUSIONS.

(1) It is shown that lime-sulphur solution is a complex solution, containing many compounds, the presence of which is generally overlooked.

(2) It is shown that in the zinc chlorid method all compounds that can interfere with the titration of thiosulphate sulphur (excepting, of course, traces of sulphite) are precipitated by the addition of ammoniacal zinc chlorid solution, or are rendered innocuous by the neutralization of the filtrate with hydrochloric acid.

(3) It is shown that in the iodin titration method such compounds will markedly affect the results obtained in the titrations, more especially in the titration for thiosulphate sulphur.

(4) A theory is advanced explaining the discrepancies observed in the determined and in the calculated values for lime, whether calculated from results obtained by the iodin titration or by the zinc chlorid method.

RECOMMENDATIONS BY THE ASSOCIATE REFEREE.

I. Lime-Sulphur Solutions.

It is recommended—

(1) That the method for *total sulphur* be changed to read as follows:

Weigh accurately 10 grams of the solution and make to 250 cc. with carbon-dioxid-free water. Transfer a 10 cc. aliquot to a 400 cc. beaker, add about 3 grams of sodium peroxid, cover immediately with a watch glass and warm on the steam bath, with frequent shaking, until all the sulphur is oxidized to sulphate, adding more sodium peroxid if necessary. (Instead of sodium peroxid, hydrogen peroxid may be employed, in which case first add 3 cc. of a concentrated (1:1) solution of sodium hydroxid. In either case carefully test all reagents for sulphur, and if present, make corrections accordingly.) Dilute, acidify with hydrochloric acid, evaporate to dryness and filter to remove silica. Dilute filtrate to 300 cc., add 50 cc. of concentrated hydrochloric acid (see *J. Amer. Chem. Soc.*, 1911, **33**: 844), heat to boiling, and precipitate, stirring constantly with a 10 per cent solution of barium chlorid. This should be added at such a rate that about 4 minutes are required in running in the amount necessary (11 cc. for 1 gram of barium sulphate); the rate is best regulated by attaching a suitable capillary tip to the burette containing the barium chlorid solution. Evaporate the whole to dryness on the steam bath (this may be done immediately after precipitation), take up with hot water, filter through paper,

[1] Bur. Chem. Bul. 162, p. 41.

wash until the washings are free from chlorid, ignite very carefully so as to obviate reduction, and heat to constant weight over a Bunsen burner. Calculate sulphur from the weight of barium sulphate, using the factor: Wt. $BaSO_4 \times 0.13738$ = Wt. S.

(2) That the method for *sulphid sulphur* be changed to read as follows:

Dilute 25 cc. of the solution, prepared as for total sulphur, to about 100 cc. and add ammoniacal zinc chlorid solution (prepared by dissolving 50 grams of pure zinc chlorid in water and adding ammonia in sufficient quantity to redissolve the precipitation first formed) until the sulphid is all precipitated, as will be shown by adding a drop of the clear solution to a few drops of nickel sulphate solution. Filter immediately, wash precipitate thoroughly and transfer, together with the filter paper, to a beaker. Cover with water, disintegrate with a glass rod and add about 3 grams of sodium peroxid, keeping the beaker well covered with a watch glass. Warm on the steam bath with frequent shaking until all the sulphur is oxidized to sulphate. (In case hydrogen peroxid is used as the oxidizing agent treat filter containing zinc sulphid with a concentrated solution of sodium hydroxid, warming on the steam bath, before adding the peroxid.) Make slightly acid with hydrochloric acid, filter to remove filter paper, wash thoroughly with hot water, and determine sulphur in the filtrate exactly as given under total sulphur.

(3) That the method for *thiosulphate sulphur* be changed to read as follows:

Dilute 50 cc. of the solution prepared as for total sulphur to about 75 to 100 cc. in a 200 cc. graduated flask. Add ammoniacal zinc chlorid until in slight excess and make to mark. Shake thoroughly and filter through a dry filter. To 100 cc. of the filtrate add Methyl Orange and exactly neutralize with dilute hydrochloric acid. Titrate this solution with standard iodin solution (approximately twentieth-normal), using a few drops of starch paste as indicator. From the number of cubic centimeters of iodin solution used, calculate the thiosulphate sulphur present. The value of the iodin solution being given in terms of arsenic trioxid, use the factor: $As_2O_3 \times 1.29628$ = thiosulphate S.

(4) That the method for *sulphate sulphur* be changed to read as follows:

To the solution from the determination of thiosulphate add 2 or 3 drops of hydrochloric acid, precipitate in the cold with barium chlorid solution, allow to stand over night, filter, and from the weight of barium sulphate calculate sulphur and report as sulphate sulphur.

(5) That total *lime* be determined as follows:

To 25 cc. of the solution prepared as for total sulphur, add 10 cc. of concentrated hydrochloric acid, evaporate to dryness on the steam bath, take up with water and a little hydrochloric acid, warming until all the calcium chlorid is dissolved and filter from sulphur and any silica that may be present. Ignite filter containing filtered sulphur, take up in a little dilute hydrochloric acid, and filter through a small filter into original filtrate. Oxidize filtrate by boiling with a little concentrated nitric acid, make ammoniacal, filter from iron and aluminum if present, heat to boiling and precipitate with ammonium oxalate solution. Filter and heat to constant weight by means of the blast lamp.

A SHORT METHOD FOR THE ANALYSIS OF A LIME-SULPHUR SOLUTION.

By S. D. Averitt.

The writer has found that an analysis of a lime-sulphur solution sufficiently accurate for commercial work may be made in about two hours. This is accomplished by weighing directly the precipitated sulphur from the iodin titrations as given in the report on insecticides this year, and estimating the sulphate and sulphite sulphur as precipitated in the iodin methods by the degree of turbidity. If the sulphate and sulphite sulphur are precipitated in not more than 50 cc., the estimation after a little practice is quite accurate, never differing more than 0.02 or 0.03 per cent from the determined value. The most rapid and accurate method of weighing the sulphid sulphur is as follows:

Wash a 7 cm. ashless filter several times with suction, dry thoroughly in the water oven; put in a weighing bottle and weigh at once. Filter the sulphid sulphur on this weighed filter, washing thoroughly, drying and weighing in the bottle as before. The difference in weight is the sulphid sulphur.

During the first drying of the filter the titrations with iodin are made, 2 or 3 drops of dilute hydrochloric acid added, the solution placed on the waterbath for a few minutes (do not heat above 40° or 50°C). When sulphur collects, it is ready to be filtered. To the filtrate and one washing (the whole should not be over 40 or 50 cc.) add 2.5 cc. of 10 per cent solution of barium chlorid, shaking thoroughly. Compare the turbidity with a standard solution in the same volume.

The following table shows the comparison of the sulphid sulphur weighed directly and determined as barium sulphate on the present association samples:

Comparison of sulphid sulphur weighed directly and as barium sulphate.

SAMPLE 1 WEIGHED AS		SAMPLE 2 WEIGHED AS	
Sulphur	Barium sulphate	Sulphur	Barium sulphate
5.83	5.82	5.86	5.88
5.83	5.89	5.92	5.92
5.78	5.77	5.80	5.87
....	....	5.80	....
Average, 5.81	5.82	5.84	5.89

On a concentrate the sulphid sulphur by difference was 23.22 per cent; weighed as sulphur 23.22 per cent and 23.14 per cent, average 23.18 per cent.

The writer has found this method of weighing the sulphid sulphur just as accurate as weighing it as barium sulphate and the total sulphur as the sum of the sulphid, thiosulphate, and sulphate sulphur never differs over 0.10 or 0.15 per cent from the total sulphur as determined, and the time saved outweighs the small loss of accuracy.

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON WATER.

By W. W. Skinner, *Referee.*

The work on water analysis for the past year was confined to a study of the proposed methods for strontium, iodin, and bromin. A sample was sent to each of nine chemists and reports have been received from six, three of whom represent the Water Laboratory of the Bureau of Chemistry. The sample was known to contain in the aliquot taken for analysis approximately 160 mg. of calcium, 31 mg. of strontium, 0.25 mg. of iodin, and 3.25 mg. of bromin. According to the method, the differences between the total oxids and the strontium oxid calculated from the strontium sulphate determined, is the value for calcium oxid. The results reported are very satisfactory.

Results on water analysis.
(mg.)

ANALYST	CALCIUM BY DIFFERENCE (Ca)	CALCIUM DIRECT (Ca)	STRONTIUM (Sr)	IODIN (I)	BROMIN (Br)
1	160.00	157.93	[1]19.90	[1]0.07	2.68
	159.40	156.51	[1]18.90	....	.....
2	[1]167.00	......	28.10	0.21	2.00
3	158.10	149.36	31.10	0.15	3.59
	157.70	147.65	31.80	0.15	3.20
	......	......	.....	0.14	3.36
4	161.90	160.50	28.10	0.21	2.21
	160.50	160.00	30.10	0.23	2.35
	159.20	158.00	.....	....	....
5	159.70	157.40	30.70	0.14	[1]0.30
	159.40	157.70	31.20	0.15	[1]0.30
	158.20	157.80	32.60	0.15	[1]0.35
6	163.00	159.40	[1]22.40	0.22	1.95
	160.30	158.90	[1]22.50	0.22	2.48
	......	......	.....	0.25	....
Average	159.78	156.76	30.46	0.18	2.65
Theory......	160.00	......	31.00	0.25	3.25

[1] Omitted from average.

The values, as you will note in the accompanying table, under the heading "Calcium by difference," agree very well with theory. This seems to hold true irrespective of whether the strontium is low or not. Two

analysts, Nos. 1 and 6, report low results on strontium, but correct results for calcium, indicating that the probable error in the method is due to excessive washing of the oxalates causing a loss due to the solubility of calcium and strontium oxalate, especially if hot water is used; and as the strontium oxalate is the more soluble of the two, the loss is first apparent in the low results for strontium. Hildebrand[1] in his methods of rock analysis reports some work by Richards and others bearing on this and remarks that this solubility of the oxalates "needs greater attention than it ordinarily receives from analysts." If double precipitation of the oxalates is made as it should be, it is surprising to most analysts to learn how little washing is really necessary.

The column headed "Calcium direct" gives the determination of calcium after the separation of strontium. This figure has been regarded heretofore as a check on the calcium by difference, but it should be noted that these results are invariably low. The exact cause has not been determined, but it is probably due to the ether-alcohol mixture failing to dissolve all of the calcium nitrate. An interesting observation, however, is in such cases where the calcium is low by direct determination, the strontium is not necessarily high. This is no doubt due to the fact that strontium sulphate is precipitated out of the alcoholic solution, while the contaminating calcium which the ether-alcohol failed to extract remains in the solution and does not come down as sulphate. With the low reports by two of the analysts on strontium thus accounted for, the results for calcium and strontium are considered to be quite satisfactory. I have thought it advisable, however, not to recommend the adoption of the method, but to refer the matter to the referee for next year with the suggestion that further work be done with the idea of determining especially the minimum amount of washing necessary for the oxalate precipitate.

Three of the six analysts obtained results on iodin that were quite satisfactory. One result was very much and two others slightly lower than the amount known to be present. The results on bromin are only fairly satisfactory, but indicate that with care in the manipulation and experience in the determination, satisfactory results may be obtained. The colorimetric methods for iodin and bromin have given results in the laboratory of the referee that are considered satisfactory for quantities of iodin and bromin such as are usually found in waters. It is true, however, that considerable experience in the manipulation is necessary in order to get satisfactory results, especially in the case of the determination of bromin where the use of an excessive amount of chlorin water will give discordant results. Unsatisfactory results are also obtained if too much

[1] U. S. Geol. Sur. Bul. 422.

of the original solution is taken so that the carbon bisulphid contains sufficient bromin to give a distinct red color. Fading of the color under such conditions is very rapid, especially if an attempt is made to make the readings in comparison tubes. Under such conditions, and in fact generally, it has been found that for bromin the comparison can best be made in small Erlenmeyer flasks without removing the solution from which the bromin is extracted. By using a definite amount of carbon bisulphid and shaking the flask in such a manner as to bring it together in one large globule the comparison in the flask may be made quite satisfactorily. It is evident also from the results reported and from work done in our laboratory that one serious difficulty in applying the method is due to loss in extraction of the residue with alcohol, especially a loss of bromin. When the residue is not too large it is possible that satisfactory results may be obtained on the residue direct without extraction. In the Bureau of Chemistry laboratory quite satisfactory qualitative results are obtained on the water directly. While the referee is satisfied that satisfactory results may be obtained by the colorimetric method for iodin and bromin, he is of the opinion that it would be unwise as in the case of strontium to recommend these methods for adoption as official until further work has been done. It is, therefore, recommended that the referee for the next year be directed to continue the work on methods for the determination of strontium, iodin and bromin along the lines suggested.

The methods proposed two years ago and which were given their first reading for final adoption at the last meeting come up automatically for final adoption at this time. It is, therefore, recommended that the proposed methods, except those for strontium, iodin, and bromin be adopted as official.

I desire to report that the referee has taken part in the discussions of a joint committee representing the American Chemical Society, the American Public Health Association, and this association for the purpose of bringing about a greater uniformity of methods for water analysis. It has been tentatively agreed upon that the methods for mineral analysis would be considered by this association, that methods for technical analysis would be considered by the committee of the American Chemical Society, while the sanitary and bacteriological analysis would receive special attention from the American Public Health Association. This general assignment of work in addition to unifying methods, is for the purpose of avoiding duplication of effort. The arrangement is only tentative, of course, and does not prevent any one of the organizations from doing work in any of the particular phases of water analysis mentioned.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By B. B. Ross, *Chairman.*

(*Phosphoric acid, nitrogen, potash, soils, inorganic plant constituents, insecticides, water.*)

PHOSPHORIC ACID.

It is recommended—

(1) That further work be done on methods for determining total phosphoric acid in basic slag.

Approved.

(2) That further work be done on methods for determining available phosphoric acid in basic slag.

Approved.

(3) That further attention be given to the presence of iron and silica in the magnesia precipitate and that methods designed to eliminate these substances be studied.

Approved.

(4) That the methods outlined for total and available phosphoric acid be tried out with a synthetic solution representing as closely as possible a solution of the average basic slag.

Approved.

(5) That the referee for next year study the titration method for making neutral ammonium citrate solution (*J. Ind. Eng. Chem.*, 1913, **5**: 567).

Approved.

NITROGEN.

It is recommended—

(1) That the ferrous-sulphate-zinc-soda method be adopted as a provisional method and that it be further studied during the coming year.

Approved for final action as provisional in 1914.

(2) That the alkaline permanganate and neutral permanganate methods for organic nitrogen availability (Bul. 162, p. 13) be adopted as official methods and that they be printed under the respective designations of "Method for the determination of organic nitrogen soluble in alkaline permanganate" and "Method for the determination of organic nitrogen soluble in neutral permanganate."

Approval for final action as official in 1914.

(3) That the referee for next year study the Kjeldahl-Gunning-Arnold method and modifications thereof with a view to its employment for the determination of nitrogen in fertilizers and fertilizer materials.

Approved.

POTASH.

It is recommended—

(1) That further coöperation be secured in testing (1) the use of denatured alcohol for washing K_2PtCl_6, with special reference to the denaturing agents, (2) the necessity for the use of hydrochloric acid in the water extract in potash determinations.

Approved.

(2) That further work be done on the perchlorate method.

Approved.

(3) That the study of potash availability be continued another year and that the effect of decomposing green material also be studied.

Approved.

SOILS.

It is recommended—

(1) That the work on humus be discontinued and that the official method for humus and humus nitrogen be eliminated from the revised methods of analysis.

Approved.

(2) That methods for determining organic carbon and nitrogen in soils be studied during the coming year.

Approved.

(3) That further study be made of methods for obtaining aqueous soil extracts and that the reduction method for nitrates and the methods for nitrites and ammonia, as adopted for waters, be approved for soil solutions.

Approved.

INORGANIC PLANT CONSTITUENTS.

It is recommended—

(1) That no further work be done on the Schreiber method for total sulphur.

Approved.

(2) That the official method for iron and aluminum be extended to include calcium and magnesium in the presence of minute quantities of manganese.

Approved.

INSECTICIDES.

It is recommended—

(1) That the whole question of the analysis of lime-sulphur solutions be referred to a committee of review, consisting of W. F. Hillebrand, C. S. Cathcart, and H. H. Hanson, whose duty shall be to consider the reports of the work of the past four years and to undertake such additional investigations as may be necessary to reach a conclusion as to the merits

of the proposed methods, a report of their findings to be rendered at the next meeting.

Approved.

(2) That the method of digestion for water-soluble arsenic in lead arsenate (p. 75 of referee's report) be made a provisional method.

Approved.

(3) That the method published by C. C. Hedges of Cornell University (*J. Ind. Eng. Chem.*, 1909, **1**: 208), for the determination of arsenious oxid in Paris green and other insecticides, be compared by the next referee with the official method now in use.

Approved.

(4) That the Lloyd method for nicotin in tobacco and tobacco extracts (p. 76 of referee's report) be compared with the official method (Kisslings).

Approved.

WATER.

It is recommended—

(1) That the referee for next year be directed to continue the work on methods for the determination of strontium, iodin, and bromin along the lines suggested in the report of the referee.

Approved.

(2) That the methods proposed in Circular 108, except those for strontium, iodin, and bromin, be adopted as official.

Adopted, final action.

REPORT OF COMMITTEE ON AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

By C. B. Williams, *Chairman.*[1]

Since the last meeting of the association the Committee on Availability of Phosphoric Acid in Basic Slag has held two meetings, one in Atlanta on November 14 and 15, and one in Washington on January 24, and has spent much time in outlining a satisfactory plan for conducting pot experiments to study the availability of the phosphoric acid of basic slag as compared with that contained in sodium acid phosphate, double superphosphate, acid phosphate, and finely-ground phosphate rock.

During April, the directions and phosphatic materials for the pot work were forwarded to fourteen station workers who had previously indicated that they would be in a position to coöperate with the committee in the investigations. Most of these have started the work, but only a

[1] Presented by H. D. Haskins.

few, as might be expected, have been able to secure results this early. At present seven station workers are coöperating in the field experiments, an outline of which was submitted at the last meeting of the association. Other workers have indicated that they would be in a position later to take up coöperative work with the committee.

It is suggested that if possible the referee on phosphoric acid use for his basic slag studies the same slags that are being used by this committee. By thus doing it is felt that the results secured by each may prove mutually valuable.

SOURCE OF MATERIALS.

At the beginning of the investigations the committee, after much correspondence, has in its judgment secured enough of each of the different phosphatic fertilizing materials to be used in the availability studies to provide all those coöperating in the pot and in the field experiments with the same materials throughout the entire period to be covered by the investigations. It was the idea of the committee to secure for these studies lots representative of the slags that are finding their way into our markets from different European and Canadian sources. The slags and other phosphatic materials finally selected and secured for the work were of the make and source indicated:

Slag A. Manufactured by the Chemical Works of the Late H. and A. Albert, England, and secured through the Coe-Mortimer Company, New York, N. Y.

Slag B. Manufactured by the Anglo-Continental Guano Works, Antwerp, Belgium, and secured through the Nitrate Agencies Company, New York, N. Y.

Slag C. Manufactured by the Dominion Iron and Steel Works, Canada, and secured through the Cross Fertilizer Company, Sidney, Nova Scotia.

Slag D. Manufactured in Belgium by a different firm from that manufacturing Slag B; secured through H. J. Baker and Brother, New York, N. Y.

Ground blue phosphate rock. Mined at Gordonsville, Tenn., and secured through the Robin Jones Phosphate Company, Nashville, Tenn.

Acid phosphate. Manufactured by and secured through the Caraleigh Phosphate and Fertilizer Works, Raleigh, N. C.

Double superphosphate. Manufactured by the American Agricultural Chemica Company, Boston, Mass., and secured through the Coe-Mortimer Company, New York, N. Y.

FINENESS AND COMPOSITION OF MATERIALS.

These materials secured for the coöperative experiments had the following average fineness and composition:

Fineness and composition of materials.

MATERIALS	FINENESS				PERCENTAGE OF TOTAL PHOSPHORIC ACID	PERCENTAGE OF AVAILABLE PHOSPHORIC ACID[1]	PERCENTAGE OF MOISTURE
	Percentage through round-holed sieve		Percentage through square-holed sieve				
	1 mm.	½ mm.	¼ mm.	$\frac{1}{10}$ mm.			
Slag A	99.86	99.31	97.28	65.36	18.06	15.87	0.19
Slag B	99.81	98.42	95.01	73.17	17.84	14.74	0.29
Slag C	99.52	98.14	94.14	68.43	13.03	13.25	0.28
Slag D	99.16	96.50	91.10	67.34	15.57	14.98	0.30
Phosphate rock	99.65	99.45	95.80	72.82	29.40	.....	....
Acid phosphate	.....	.....	.....	.....	19.49	17.82	....
Sodium phosphate	.....	.....	.....	.....	20.87	20.87	....
Double superphosphate	.....	.....	.....	.....	46.25	46.02	....

[1] Available phosphoric acid determined in slags by Wagner's 2-per cent citric acid method and in other materials indicated by the official ammonium citrate method.

DIRECTIONS FOR CONDUCTING POT EXPERIMENTS.

NATURE OF SOIL.

If the field work is being undertaken at the same time, use for the pot experiments the surface soil after the phosphoric acid has been exhausted in the field by growing of crops. Fill all pots with well-mixed soil taken from a number of places on Plats 5 and 34 (see fig. 1 opposite, p. 50 of Bur. Chem. Bul. 162); those who have access to fields that are known to be deficient in phosphoric acid may use such soils in place of what is recommended. The experimenter should prove beyond a doubt that the soil is deficient in phosphoric acid, even though this had been indicated in previous field tests. The thorough breaking up and mixing of the soil in preparing it for pot work, together with the liberal quantity of lime which is later recommended, will unquestionably render available some of the inert phosphoric acid in the soil. In such a soil it probably would not be as difficult to deplete the phosphoric acid as would be the case if the soil were taken from a field where no previous efforts had been made to exhaust the soil of this constituent. Some time might therefore be saved in choosing a soil which was deficient in phosphoric acid.

The experiment is to be conducted with the same soil and is to be carried on in two main divisions. In the first, some leguminous crop such as clover, vetch, or cowpeas, is to be grown without fertilization (except lime), the fertilizer being applied subsequently in intimate contact with the green crop after it has been passed through a cutter and mixed with the soil in the respective pots. In the second division the soil in the pots is to remain in a fallow condition, after an application of lime, during the growth of the legume. In one of the divisions the legume is grown and turned under in order to study what is thought to approach more nearly practical soil requirements for best farm results with some of the phosphate materials under investigation. Subsequent to the production of the legume selected for growth in the first division of pots during the preliminary period, the soil of all the pots of both divisions of the experiment should be treated at the same time and in the same manner. The seeding of the legume should be uniform for all the pots that are to grow this crop.

TAKING SOIL.

Take soil for the pot experiments to the depth of 7 inches, excluding stubble and other undecomposed organic material and stones. On a sample of the mixed soil as weighed into the pots, determine the loss upon air-drying, pass the air-dried soil through a 3 mm. sieve, determine the percentage of coarse material, select a 2-quart sample from the mixed, sieved material and dry it for 8 hours at 70°C., determining the loss of water. Preserve for possible future analysis.

FILLING POTS.

Fill the pots from the thoroughly-mixed soil, placing equal quantities by weight in each pot so that after the soil has been compacted its surface will be within an inch of the top. Those who use pots over a foot in depth may, if they prefer, fill the excess depth at the bottom with subsoil, or they may, in case of pots of any depth, use the surface soil on top to the depth at which it occurred in the field and use subsoil for the remainder at the bottom. The lime and fertilizer applications should be mixed with the surface soil and should be made on the basis of air-dry surface soil, exclusive of subsoil. If possible, all pot tests in the four series should be run in duplicate.

APPLICATION OF LIME.

The lime should preferably be added on the basis of analytical data secured in accordance with the Veitch method (*J. Amer. Chem. Soc.*, 1902, **24**: 1120–1128; Bur. Chem. Bul. 73, p. 136) using for this purpose a portion of the oven-dried sample already mentioned, having first passed this portion through a 1 mm. sieve. Determine the relation of this sieved subsample to the surface soil as weighed into the pots, as well as its relation to the main oven-dried sample. Add per air-dried soil, in excess of the lime requirements as determined by the Veitch method, calcium carbonate at the rate of about 0.10 per cent for L and 0.15 per cent for L_x.

APPLICATION OF NITROGEN.

For applications of nitrogen add for air-dry soil, 0.06 per cent of nitrogen from dried blood and 0.01 per cent from nitrate of soda, for N, and 0.09 per cent of nitrogen from blood and 0.015 per cent nitrogen from nitrate of soda, for $N_{1\frac{1}{2}}$.

APPLICATION OF POTASH.

For the application of potash, add for air-dry soil, 0.10 per cent of potash for K, and 0.15 per cent of potash for $K_{1\frac{1}{2}}$, of low grade sulphate of potash.

APPLICATION OF PHOSPHORIC ACID.

For the application of phosphoric acid, add for air-dry soil, 0.007 per cent of phosphoric acid for $P_{\frac{1}{2}}$, 0.014 per cent of phosphoric acid for P, 0.021 per cent of phosphoric acid for $P_{1\frac{1}{2}}$, and 0.028 per cent of phosphoric acid for P_2 of the different phosphatic materials indicated.

FERTILIZERS.

If, during the growth of the plants, it appears that those which receive sodium phosphate or double superphosphate together with $N_{1\frac{1}{2}}$ and $K_{1\frac{1}{2}}$ are growing better than those with N and K, all pots which received N and K should have added to them an equal amount of a solution of nitrate of soda and low grade sulphate of potash and those which had received $N_{1\frac{1}{2}}$ and $K_{1\frac{1}{2}}$, 50 per cent more than this, since it is necessary in an experiment of this kind to have the N and K present in optimum amounts.

Owing to the varying requirements of different soils it is, of course, only possible for the committee to suggest what should be added. Those who know the specific requirements of their soils, should feel free to vary the applications suggested. It should be borne in mind, however, that in pot experimentation, especially if the plants are allowed less feeding area than in the field, the applications must be very liberal.

It is realized that the requirements of the different kinds of crops are not the same, but it is hoped that the applications suggested above are liberal enough to cover each case. It is especially difficult for the committee to suggest applications of phosphoric acid suitable under different conditions, since it is desired to have the applications of $P_{\frac{1}{2}}$ in sodium phosphate and double superphosphate below the optimum requirements of the plants, as indicated by the larger crop which should be secured by P and $P_{1\frac{1}{2}}$.

The suggested applications of lime are liberal in order to remove the possibility of the basic material of the slags exerting any beneficial influence either on the reaction of the soil or in connection with the liberation of plant food ingredients.

It is advisable to mix fertilizing materials with the soil, then moisten thoroughly and uniformly and allow to stand for two weeks in advance of seeding.

CROPS.

For the field experiments Japanese millet and dwarf Essex rape have been selected. In the pot experiments millet or spring wheat and rape should be used. Add an equal weight of good seed to each pot, thin to the best plants, finally allowing not less than nine square inches to each rape plant and about four squares inches to each millet or wheat plant, making sure that in the case of each crop an equal number of plants are left in each pot.

WATERING THE PLANTS.

Owing to varying conditions it is impossible to make suggestions regarding the watering except to call attention to the fact that at a given time approximately equal amounts of water should be added to plants of similar size.

HARVESTING.

Report the following data: Crops used; character of soil; depth of surface soil in the field; per cent of calcium carbonate required, according to the Veitch method, by the dry soil finer than 1 mm.; per cent of this fine soil in the oven-dried soil finer than 3 mm., and in the soil used in the pots when air-dried; kind and dimension of pots; depth of soil and of subsoil in pots; weight of surface soil in air-dry condition per pot; per cent material coarser than 3 mm. in air-dry soil; time of planting; number of plants per pot; time of harvesting; state of maturity; method of drying the crops; weight of crop from each pot; variations from the suggested directions.

SUPPLY OF MATERIALS.

The sodium phosphate, double superphosphate, acid phosphate, Thomas slag phosphate and ground (blue) phosphate rock together with the analyses of same, will be supplied by the committee to those coöperating in the experiments. These analyses are to be the basis of the phosphatic materials.

FERTILIZER APPLICATIONS PER POT.

N, 0.06 per cent of nitrogen from dried blood and 0.01 per cent from nitrate of soda.

K, 0.10 per cent of potassium oxid from low grade sulphate of potash.

P, 0.014 per cent of phosphoric acid respectively from the different phosphatic materials indicated.

L, 0.10 per cent of calcium carbonate plus that required by the Veitch test.

L_x, 0.15 per cent of calcium carbonate plus that required by the Veitch test.

Run the pot experiments with each crop in two main divisions. After lime is applied and before fertilizer treatment begins with any crop, on the first division a leguminous cover crop is to be grown and to be turned into the soil. During this period, the second division is to remain fallow after adding lime. In the case of each division, the following fertilizer treatments are recommended for the respective groups, each of which is to run in four series:

Group	1	NKL.	
	2	NKL.	
	3	$NP_{\frac{1}{2}}KL$	Phosphoric acid from Slag A.
	4	$NP_{\frac{1}{2}}KL$	Phosphoric acid from Slag B.
	5	$NP_{\frac{1}{2}}KL$	Phosphoric acid from Slag C.
	6	$NP_{\frac{1}{2}}KL$	Phosphoric acid from Slag D.
	7	$NP_{\frac{1}{2}}KL$	Phosphoric acid from acid phosphate.
	8	$NP_{\frac{1}{2}}KL$	Phosphoric acid from ground (blue) phosphate rock.
	9	$NP_{\frac{1}{2}}KL$	Phosphoric acid from sodium phosphate.
	10	NPKL	Phosphoric acid from Slag A.
	11	NPKL	Phosphoric acid from Slag B.
	12	NPKL	Phosphoric acid from Slag C.
	13	NPKL	Phosphoric acid from Slag D.
	14	NPKL	Phosphoric acid from acid phosphate.
	15	NPKL	Phosphoric acid from ground (blue) phosphate rock.
	16	NPKL	Phosphoric acid from sodium phosphate.
	17	$NPKL_x$	Phosphoric acid from sodium phosphate.
	18	$N_{1\frac{1}{2}}PK_{1\frac{1}{2}}L$	Phosphoric acid from sodium phosphate.
	19	$NP_{1\frac{1}{2}}KL$	Phosphoric acid from sodium phosphate.
	20	NP_2KL	Phosphoric acid from ground (blue) phosphate.
	21	$NP_{1\frac{1}{2}}KL$	Phosphoric acid from double superphosphate.
	22	NPKL	Phosphoric acid from double superphosphate rock.

The complete pot experiments comprise the following four series.

1. Millet or wheat (spring) after previous growth of legume turned into the soil.
2. Rape after previous growth of legume turned into the soil.
3. Millet or wheat (spring) without previous growth of legume, but after fallowing.
4. Rape without previous growth of legume, but after fallowing.

If only one pot is allowed to a single treatment it will require not less than 88 pots for carrying out the entire scheme of experiments and it is very important to carry out the full line of investigations in duplicate. It is especially important in Groups 9, 16, 21, and 22 that at least two pots (and preferably three) be used for each treatment.

A resolution was introduced by C. H. Jones on behalf of the executive committee that three associate referees be appointed as follows: (1) For the special study of the Kjeldahl method for the determination of nitrogen; (2) for the study of alkali in soils; and (3) on feed adulteration. The resolution was adopted.

REPORT OF COMMITTEE ON FOOD STANDARDS.

By Wm. Frear, *Chairman.*

The committee on food standards has been marking time this year, as it has been for a year or two past. In the whole history of the standards work it has been made absolutely manifest that to secure a final adoption and general acceptance of any work for standardization all official interests that could in any way be concerned in the final use of these standards must have opportunity for conference in the preparation of the standards. Such co-relation of the various officials interested and needing to use standards was for a time impracticable. While there was need for work it would be unfortunate to have it carefully done and yet but partly accepted or not accepted at all because of the lack of proper representation in the body charged with the work of making standards. So far as this association is concerned, this committee was fully authorized, but as for some years we had been associated with interests that needed to be considered, and since it was impossible for us to secure for a time the active assistance from those other organizations, this committee has not attempted to go ahead with the standards work. There is now, I am pleased to say, some prospect of coöperative work such as ought to be done. Unfortunately I was not present at the conference at which that united action was made a subject of resolutions, and, therefore, I am unable to report in any official way from that body to this, but I assume that a presentation of that matter will be made.

REPORT OF COMMITTEE ON EDITING METHODS OF ANALYSIS.

By J. K. Haywood, *Chairman.*

I have never called a meeting of the committee on editing methods of analysis, and I am afraid it was an error on my part not to do so. It was my understanding that there was already a committee to take care of the revision of methods, and that a mistake had been made in appointing our committee. There was already a committee on recommendation of referees and revision of methods; I was the first chairman of that committee four or five years ago, and at that time it was the idea of a good many that that committee was going to handle the revision. I think the committee on recommendation of referees and revision of methods is the proper one to revise the methods, because of its familiarity with the subject. Therefore, it was my thought that the appointment of this special committee was possibly a mistake on the part of the chair, so I did not take any action, and thought the subject would be referred to

the other committee. Now, the chair assures me that there is nothing in the resolution appointing the committee on recommendation of referees and revision of methods assigning to it the revision of methods, and if that is so, the committee on editing methods of analysis has made a mistake in not handling the matter. If the association wishes this committee to go ahead with the revision, it will be glad to do so.

REPORT OF COMMITTEE ON PRACTICABILITY OF ORGANIZING FOR STUDY OF VEGETABLE PROTEINS.

By L. L. Van Slyke, *Chairman.*

It will be useful to introduce this report with a brief historical statement. In 1901 the subject of separation of nitrogenous bodies was first added to the work of this association, and the first referee's report made in 1902, at which time the subject was subdivided into three parts: Proteins of (1) milk and cheese, (2) plants, and (3) meat. In the ten years in which the subject of vegetable proteins has been a part of our regular work, no reports were made and no work done in the years 1908, 1909, and 1911; in 1903 and 1907 the reports consisted solely of summaries of literature; it was actually reported only five times. The separation of wheat proteins has formed the chief subject of study, with the exception of one year when attention was given to barley and malt. These statements obviously indicate that little advance has been made by the association in this field and the meagerness of results suggests that a complete change of policy must be adopted, if progress is to be made. Methods of study have undergone profound changes in recent years and workers in this field have a marked advantage over the workers of ten years ago. It is believed that the association should undertake anew a study of vegetable proteins, especially in relation to devising practicable methods of separation. While we do not think it necessary here to give detailed reasons for this belief or to attempt to point out more specifically the problems and methods of attack, the following suggestions are offered as a basis for organized effort.

(1) In place of a single, transitory referee, there should be a small permanent committee, in which the personel shall remain as constant as circumstances permit.

(2) Such committee should consist of members whose special training and professional interests give them the highest degree of fitness and stimulation for the work. As chairman of this committee one name and only one suggests itself, that of T. B. Osborne, who is in a position of advantage to select other members.

(3) The permanent feature of the committee is absolutely essential to success in carrying out a systematic, effective line of work.

(4) The committee should have full power in respect to planning and executing all details.

(5) The suggestions of Mr. Osborne contained in the Report of 1912 (Bur. Chem. Bul. 162, pp. 154–159) furnish most valuable details for guidance in this work.

REPORT ON FOOD ADULTERATION.

By Julius Hortvet, *Referee.*

Recent years have witnessed many noteworthy changes both in respect to the purposes of chemical investigations affecting the control of foods and in the character of analytical methods of procedure. The enforcement of the Federal Food and Drugs Act, the extension of pure food legislation and regulation among the states, combined with the more intensive study of conditions of manufacture and distribution, have all contributed very largely, more than can be realized on momentary reflection, to a new era in that branch of applied analytical chemistry having directly under its charge the character of foods, drugs, and other articles of commerce.

A reliable choice of an analytical method of procedure now shows a decided trend toward a greater refinement in details, a stronger emphasis, and a clearer insight respecting fundamental principles and true chemical relations. It is now recognized more than heretofore that any really reliable chemical test or analytical procedure must be far beyond the elementary condition. Increased accuracy is demanded by the greater emphasis on exact definitions, true classifications, and the necessity of differentiating between products having close generic relations. There is evident a greater adaptation of methods of procedure to the nature of the material under investigation, a greater insistence on the recognition and handling of interfering conditions, and there is also a marked tendency withal toward increased reliability and a natural selection in the direction of shorter and simpler analytical procedures.

The increased forensic demands of the past few years have influenced greatly the study of official methods of analysis and have stimulated the development of new methods in many directions. This has been illustrated very strikingly with such products as vinegars, flavoring extracts, baking chemicals, canned goods, dairy products, brewed beverages, and coloring matters. There has been something akin to a revolution in the manufacturing, shipping, and marketing of food products, and the attending changes have affected to a considerable degree the study and develop-

ment of the analytical processes. Methods which only a few years ago served fairly well have now become inadequate or entirely obsolete. Such conditions as the increasing variety of vinegars made from various sugar wastes and sugar-containing substances, the identification of certified and uncertified coal-tar dyes, the determination of the character of the mash from which a certain variety of beer is brewed, the complications arising from the use of the homogenizer in the manufacture of milk and cream products, the changes attending cold storage of meats and eggs, and a multitude of other problems compared with which these illustrations are only a typical few have to be contended with now.

The associate referees of the present year have shown to a degree comparing favorably with the work of preceding years, faithful attention to the study of proposed methods and modifications and to the furtherance of the wishes of the association as expressed at the last meeting. Details of the results accomplished will be adequately presented as the referees' reports are read, but a few salient features of these reports may be appropriate.

An examination of the report of the referee on heavy metals gives an impression of the progress now making toward accurate determinations in cases where metallic impurities are present in very minute quantities. It is impossible, however, to forego the suggestion that there is to some extent an overstepping tendency to experiment with colorimetric methods, notably in certain instances where obviously there can be little gained in respect to accuracy or rapidity of manipulation. These attempts, nevertheless, are not to be discouraged. In connection with the report on lead, there is, so far as one can judge from the reports and comments of the collaborators, a prevailing tendency in favor of a gravimetric procedure.

Too great importance cannot be attached to such work as that which has been carried out by the referee on water in foods. The systematic trying out of various dehydrating agents under different conditions is a line of work that is well worth attention and should be continued during the coming year. The same statement applies also to efforts on the part of collaborators on other subjects in which a similar investigation has been attempted.

The referee on colors has undertaken a most extensive scheme of collaborative work, a plan which apparently will lead to a complete revision of existing outlines of procedure. As a matter of valuable training, the detailed directions and outlines of the referee should be in the hands of all food chemists who are engaged especially on color work and who can arrange their time so as to carry out the plan of the work satisfactorily.

In connection with the work on wine, it has been suggested that there is urgent need of more information regarding the composition and prop-

erties of the so-called "fixed acids," with a view toward extending the abilities of the association beyond the handling of the ingredient which has heretofore been investigated as tartaric acid.

The referee work on beer, though confined to a study of the methods for phosphoric acid, is very important. This report represents a neat piece of work and is a good model illustrating a kind of collaborative work much needed in order to perfect the methods. Accurate methods for beer analysis are also especially in demand now owing to the exigency which has recently arisen following the enforcement of regulations affecting the labeling of brewed or so-called malt beverages.

A decided preference has developed in favor of the glycerin saponification method in carrying out the titer test in fats and oils. Also, a study of the Emery method for detecting beef fat in lard seems to have come to a favorable conclusion. If further work on this method is to be carried out, a study of comparative tests by the Belfield method is suggested both as a reliable check method and as a method which can be further perfected.

The work on methods for meat and fish is noteworthy for the successful attempts which have been made to overcome unusual difficulties, particularly in respect to the preparatory treatment of the material in the determinations of starch and sugar. The evolution of the Folin ammonia method is interesting and affords an illustration of what has been said regarding the tendency toward the adoption of shorter procedures and simpler details.

The referee on flavoring extracts has brought out some interesting facts respecting the influence of certain interfering substances in the application of Folin's test for vanillin. These considerations should be taken up and further study of the test is recommended. The reports of analyses of authentic vanilla extracts constitute a valuable and very practical feature of the report, and this suggests the importance of contributing reliable data in all cases where such data may be available for the use of the committee on standards.

The report of the referee on inorganic phosphorus covers two years of collaborative work, and for that reason affords a clearer view than would otherwise be possible of the considerable progress accomplished in this difficult field. This report is a good model of collaborative work, and while the subject-matter may not be directly classed under the general caption of Food Adulteration, the report is noteworthy, not only as a valuable contribution in its own field, but as one of a most helpful kind deserving a careful study on the part of all food analysts. The study of methods on inorganic phosphorus in plant and animal substances should be heartily endorsed and provision made for its continuation during the coming year.

The reports of the associate referees show the importance of experience as a qualification on the part of the collaborators. Too infrequently has it occurred that the same collaborators continue in a given line of work more than a year. Some arrangement is desirable whereby the referees may be assured of the continued assistance of experienced collaborators, and to this end much improvement may result if trained analysts are encouraged to continue a line of study until they as well as the referees feel reasonably satisfied with the conclusion of an investigation. A large proportion of volunteering collaborators fail to report; this is in itself a matter of some concern, for, generally speaking, "The readiness of doing doth express no other but the doer's willingness." Quality of work more than quantity is however to be emphasized, and it is well to point out that many failures to report may be owing to an inadequate appreciation on the part of the volunteers of the true nature and importance of the collaborative work to be undertaken.

In conclusion I wish to state my appreciation of the efforts on the part of the associate referees and their collaborators in the study of proposed methods and in the direction of new lines of investigation. There has been manifested a decided interest on the part of all and a hearty willingness to comply with the requests of the referee on food adulteration and the committee on recommendations of referees and revision of methods. We have in the majority of cases received copies giving full reports of work accomplished and in the main the abstracts which have been furnished have served their purpose well. In conclusion, thanking my associates for their interest and hearty coöperation, I am pleased to have these referee reports submitted to the association.

REPORT ON COLORS.

By W. E. Mathewson, *Associate Referee.*

The work done on colors this season has comprised the examination by the collaborating analysts, of a number of samples of colored imitation liquors and further work by the associate referee on the solubilities and characteristic reactions of the common dyeing matters.

The preliminary treatment of samples suspected of being colored consists usually in the extraction of the coloring matter with some solvent by which it is separated from most of the food material and obtained in a solution suitable for further examination. This gives no special difficulty with foods such as candies, sirups, and beverages, but with a few classes, as macaroni and oils, the methods for this step are still very unsatisfactory. This problem has not been taken up, at least directly, this year, as until the solubilities of the colors are better known, it can hardly be studied systematically.

COÖPERATIVE WORK ON COLORED CORDIALS.

Five samples of colored cordials were sent to the collaborating chemists, together with copies of the report of last year's work and a set of tables designed to be supplementary to the procedure for examination of color mixtures and to provide the first draft for a systematic, coherent treatment of the subject. The essential features of this table are described in the latter part of this report. The samples were colored as follows, the percentage showing the amount of commercial dye in the mixture.

No. 1.	0.01 per cent Ponceau 3R	(S. & J. No. 56).
	0.01 per cent Naphthol Yellow S	(S. & J. No. 4).
	0.01 per cent Orange I	(S. & J. No. 85). (Contained about 4 per cent of Orange II as subsidiary dye.)
No. 2.	Cochineal	(S. & J. No. 706).
	0.01 per cent Brilliant Scarlet	(S. & J. No. 106).
No. 3.	0.01 per cent Auramin	(S. & J. No. 425).
	0.01 per cent Rhodamin B	(S. & J. No. 504).
No. 4.	0.01 per cent Indigo Carmine	(S. & J. No. 692).
	0.01 per cent Palatine Scarlet	(S. & J. No. 53).
	0.01 per cent Eosin	(S. & J. No. 512).
No. 5.	0.01 per cent Guinea Green B	(S. & J. No. 433).
	0.01 per cent Metanil Yellow	(S. & J. No. 95).

About three weeks after mixture No. 4 was made, it was noted that the color had changed from bluish violet to orange red, and apparently in all cases this had taken place with the analyst's samples before they had been examined. Most of the chemists used the table sent, together with personal notes and the various standard works.

E. H. Grant reported that he had much trouble with the green dye in No. 5 and called attention to the fact that Auramin is decolorized and destroyed by caustic soda, a point not brought out in the table. The Guinea Green in mixture No. 5 was the commercial dye, which being produced by chemical reactions that give rise to considerable amounts of subsidiary products, is less definite in composition than most of the other coloring matters. It had been previously analyzed and found to give a large fraction of coloring matter similar in solubility to Light Green S F Yellowish. Distinguishing these dyes was further complicated by the fact that commercial Light Green S F Yellowish contains small amounts of subsidiary dyes similar to or identical with Guinea Green B. H. L. Lourie states that he considered this differentiation the most difficult of any in connection with the samples. R. W. Balcom used a systematic procedure by which the colors are divided into groups, the solu-

COLORING MATTERS REPORTED BY COÖPERATORS.

Analysts	*Sample 1*	*Sample 2*	*Sample 3*	*Sample 4*	*Sample 5*
C. K. Glycart, Chicago, Ill.	Ponceau 3 R Naphthol Yellow S Orange I	Cochineal Brilliant Scarlet	Auramin Rhodamin B	Palatine Scarlet Eosin	Guinea Green B Metanil Yellow
H. O. Fuller, E. B. Wettengel, T. M. Rector, Washington, D. C.	Ponceau 3 R Naphthol Yellow S Orange I Orange II	Cochineal Brilliant Scarlet Orange IV	Auramin Rhodamin B	Ponceau 3 R Eosin	Orange IV Guinea Green B[1]
C. S. Brinton, Philadelphia, Pa.	Ponceau 3 R Naphthol Yellow S Orange I	Cochineal Brilliant Scarlet	Auramin Rhodamin B	Palatine Scarlet Eosin	Guinea Green B Metanil Yellow
E. H. Grant, Washington, D. C.	Naphthol Yellow S Orange I Amaranth	Brilliant Scarlet Cochineal	Auramin Rhodamin B	Ponceau 6 R Eosin	Metanil Yellow Guinea Green B
C. F. Jablonski, New York, N. Y.	Ponceau 3 R Naphthol Yellow S Orange I	Cochineal Brilliant Scarlet	Auramin Rhodamin B	Palatine Scarlet Eosin	Guinea Green B Metanil Yellow
H. W. Haynes, Detroit, Mich.	Ponceau 3 R Orange I	Brilliant Scarlet Cochineal[1]	Rhodamin B Auramin[1]	Palatine Scarlet Eo in	Metanil Yellow Guinea Green B
H. L. Lourie, New York, N. Y.	Ponceau 3 R Naphthol Yellow S Orange I Orange II	Brilliant Scarlet[1] Cochineal	Auramin Rhodamin B	Palatine Scarlet Eosin	Light S. F. Yellowish Metanil Yellow
R. W. Balcom, Nashville, Tenn.	Ponceau 3 R Naphthol Yellow S Orange I	Brilliant Scarlet Cochineal	Rhodamin B	Eosin Fast Red E	Metanil Yellow Guinea Green B

[1] Second report on identification of this dye.

bilities applied being essentially those given in the tables sent. The details and methods for identification were supplied largely from his own notes.

SOLUBILITIES OF COLORS.

In any systematic separation of mixtures of the dyeing substances by shaking out their solutions with immiscible solvents, the components will be separated into a number of groups. A knowledge of the solubility of colors shows to the analyst at once what must be looked for in any given group. This makes it desirable to have, first, a table showing the dyes arranged in the order of their solubility toward the solvents most important in the analysis; and second, their important chemical properties tabulated in the same way so that the chemist may compare at once the behavior of the different members of a given group. The number of different coloring matters described in any scheme must necessarily be limited to a small percentage of the thousands known. B. C. Hesse in 1907 found some seventy coal-tar dyes offered for sale in America for food purposes (Bur. Chem. Bul. 147) and this list has been made the basis of the present table. It includes most of the dyes permitted in France and conforms closely to the group of colors at present sold in Europe for use in food products. In addition, such other dyes have been described in the table as have actually been found in food products by analysts and finally, a few have been added to represent several important classes of chemical compounds. The solubilities have been determined for the most part with commercial dyes and are therefore given tentatively. It will be apparent however, that subsidiary colors of different solubility when present in but small amounts cannot affect the observations greatly as they might do in chemical tests.[1] The aqueous solutions before shaking with the solvents were so made as to contain 0.01 per cent of commercial color. The treatment of the natural colors, most of which are mixtures, is, it must be confessed, very unsatisfactory.

[1] The data given for amyl acetate was obtained using the c. p. product of well known manufacturers. Such amyl acetate has since been found to be very variable in solvent power, and analyses made by A. L. Burns in the New York laboratory of a number of samples of the c. p. grade furnished by several of the large manufacturing firms showed in some cases as low as 75 per cent amyl acetate by saponification, the impurity being presumably chiefly amyl alcohol. No considerable amount of free acetic acid was found. Amyl acetate was selected as a solvent because it seemed practically the only one cheap enough to be available and of properties intermediate between those of amyl alcohol and ether. Mixtures of solvents such as ether and amyl alcohol are open to the objection that when one component is more soluble than the other the washing changes their relative proportion. The amyl alcohol used was Kahlbaum's "iso, pyridin free." This doubtless is a mixture of isomers, but experience here has not shown any significant variation in different lots (Author, January, 1915).

In the procedure described in last year's report, any given dye will, in general, appear in several washings obtained in the fractionation. Where the maximum amount comes out, may be judged from the foregoing solubility data. It must be emphasized that the statements made apply only to very dilute solutions. A concentration of 0.01 per cent may be taken as a type.

This procedure gives the best results with the acid dyes containing phenolic hydroxyl groups and most of the common dyes used in food belong to this class. With mixture containing only permitted dyes, it affords a fairly rapid means of obtaining the colors in quite pure condition in which they may be readily identified. It is more or less unsatisfactory with the lower sulphonated triphenyl methane dyes such as Guinea Green B, and certain others as Methylene Blue, Congo Red, and Naphthol Green B. With some of the basic colors also, the extraction with ether from a strongly alkaline impure mixture is somewhat uncertain, the dyes being sensitive to alkalies and extracted with some difficulty.

Where a more careful separation must be made, it is well to begin by treating with one-fourth volume of 25 per cent salt solution, and extracting a few times with amyl alcohol. (In all cases in these extractions, any separated solid matter should be considered as belonging to the aqueous layer.) The amyl alcohol is washed with 5 per cent salt solution, then evaporated to dryness on the water bath, the residue moistened with a drop of alcohol and taken up with water. This solution may be made alkaline and the basic dyes removed with ether. Hydrochloric acid is then added until it is about normal and the eosins and lower sulphonated dyes removed with amyl acetate. The acid triphenylmethane dyes are now separated with dichlorhydrin-carbon tetrachlorid mixture. Any color remaining may be separated with amyl alcohol and this added to the amyl alcohol solution of the higher sulphonated colors obtained as follows:

Sudans and similar insoluble colors in the residue left on evaporation of the amyl alcohol extract from the sodium chlorid solution will not be taken up by water. Such a residue should be dissolved in ether. Instead of evaporating the amyl alcohol extract, the dissolved color may in most cases be removed by diluting with gasoline and washing with water (or dilute acid).

The salt solution from which the basic and the more soluble acid dyes have been removed is made strongly acid by addition of one-third to one-half volume concentrated hydrochloric acid and extracted a few times with amyl alcohol. The combined amyl alcohol extract is washed once with dilute hydrochloric acid (four to five normal) then several times with fourth-normal hydrochloric acid until the washings contain little coloring matter (the first one or two washings will in all cases contain

little color because of the acid dissolved in the solvent). The Fast Red and Ponceau dyes may now be removed by washing with water. It may be remarked here that the plan of acidifying strongly, extracting, and then washing the solvent with a more dilute acid is in nearly all cases preferable to gradually increasing the acidity and using a number of portions of solvent. Much more solvent is required in this plan, with a corresponding increase in the proportion of the accompanying impurities and in the difficulties from emulsification.

The strongly acid salt solution from which colors soluble in amyl alcohol have been removed is neutralized with sodium hydroxid or ammonium hydroxid, then made very slightly acid with hydrochloric acid and shaken out a few times with dichlorhydrin to take up strongly sulphonated triphenylmethane dyes. Acid Fuchsin will remain in the aqueous mixture and may be taken up with anilin, or on making strongly acid with phenol. The dichlorhydrin solution is washed with a little 5 per cent salt solution, then diluted with benzol or carbon tetrachlorid and the dye removed with water.

When Naphthol Green B is present, the salt solution after extracting the basic dyes cannot be made strongly acid, as this would quickly destroy the nitroso color. When its presence is suspected, the neutral salt mixture may be first extracted with dichlorhydrin, washed once with benzol to remove the dissolved solvent, then made half-normal with hydrochloric acid and shaken out with anilin (it is best to add the solvent before the acid). From the anilin solution, the dyes may be fractionated as indicated in the solubility table.

The commercial acid yellows (S. & J. Nos. 8 and 9) are mixtures of compounds of different degrees of sulphonation. This and their difficult solubility in amyl alcohol renders their separation troublesome, and from mixtures containing much organic matter they are often best separated by wool. Quinolin Yellow, and in general most dyes made by direct sulphonation of the coloring matter, are likely to yield fractions of different solubilities.

The final separation of mixtures of dyes of rather similar solubility will, of course, depend on the selection of some pair of solvents in which they show a decided difference. A fixed plan of analysis beyond a certain point will scarcely be followed as the shade, behavior with acids, and other apparent or easily determined properties of the mixture, will have shown the absence of many colors. Usually a satisfactory fractionation of a pair of dyes can only be effected by the use of two to four portions of solvent and of washing liquid, following a plan similar to that used in a quantitative separation.[1]

[1] See *J. Ind. Eng. Chem.*, 1913, **5**: 26; Bur. Chem. Cir. 113.

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EXTRACTION OF DYES FROM AQUEOUS SOLUTIONS

(Statements in all cases refer to the amount of dye taken up

Color	S. & J. No.	Amyl alcohol and 5 per cent sodium chlorid solution	Amyl alcohol and dilute hydrochloric acid: 4 Normal	Normal	1/4 Normal	1/16 Normal	1/64 Normal	1/256 Normal	Dichlorhydrin and [illegible]: 5 per cent sodium chlorid	[illegible] per cent sodium [illegible]
Caramel		Little extracted.	Little extracted.	Little extracted.	Little extracted.	Little extracted.	Little extracted.			Little extracted.
Acid Magenta	462	do	Larger part not extracted.	do	do					
Light Green S F yellowish	435	do	Little extracted.	do	Very little extracted.	Very little extracted.	Very little extracted.		Larger part extracted.	Almost all extracted.
Light Green S F bluish	434	do	do	do	do	do	do		do	do
Cyanole extra	439	do	do	do	Little extracted.	Little extracted.	Little extracted.		do	do
Wool Green S	491	do	do	do	Larger part not extracted.	Larger part not extracted.	Larger part not extracted.		do	do
Patent Blue	440	Less than one-half extracted.	do						Almost all extracted	do
Nigrosin	602	Larger part precipitated.		Larger part extracted; much precipitated.	Some extracted; much precipitated.	Little extracted; much precipitated.			do	do
Ponceau 6 R	108	None extracted.	Larger part extracted.	Very little extracted.					None extracted.	[illegible]
Acid Yellow G	5	do	do	Less than one-half extracted.	Little extracted.				Very little extracted	Very [illegible]
Acid Yellow R	9	do								
Brilliant Yellow S	89	do	Larger part extracted.	Less than one-half extracted.	Little extracted.				Very little extracted	Very [illegible]
Indigo Carmine	692	do	do	About one-half extracted.	do				do	
[illegible] S	399	do	Almost all extracted.	do	do				do	
[illegible]	107	do	do	Larger part extracted.	do				Not extracted.	Not extracted.
[illegible]	106	do	do	do	do				do	
[illegible]	94	do	do	do	do				do	
Naphthol Green B	398	do	Larger part extracted.	About one-half extracted.	Less than one-half extracted.				do	
Azo Carmine BX	605	do	do	Larger part extracted.	do	Little extracted.				
Orange G	14	do		Almost all extracted.	About one-half extracted.	do				
Naphthol Black B	188	do		do	do	do				
Chromotrope 2 R	20	do		do	Larger part extracted.	About one-half extracted.	Less than one-half extracted.			
Azo Fuchsin G	93	do		do	Almost all extracted.	More than one-half extracted.	do			
Water Blue	480	do		do	Larger part extracted.	do	do	Less than one-half extracted.		
									Amyl [illegible]: 4 Normal	[illegible]
Palatine Scarlet	53	do				Larger part extracted.	About one-half extracted.	do	Very little extracted	[illegible]
Ponceau 2 R	55	do				do	do	do	do	
Ponceau 3 R	56	do				Almost all extracted.	Larger part extracted.	do	do	
Naphthol Yellow S	4	Little extracted.				do	do	Less than one-half extracted.	Larger part extracted.	Less than one-half extracted.
Palatine Red	62	do				do	do	do	Little extracted.	None extracted
Crystal Ponceau	64	do				do	do	do	Less than one-half extracted	
[illegible] L	65	do				do	do	About one-half extracted.	Little extracted	
Azo [illegible]	103	do				do	do	do	Less than one-half extracted	
Fast [illegible] L	105	do				do	do	do	Little extracted	
Azo Carmine [illegible]	604	Little extracted; much precipitated.				Larger part extracted.	do	Larger part extracted.	Little extracted, much precipitated.	Very little extracted, much precipitated.
Rosinduline 2 G	606	Almost all extracted.				Almost all extracted.	Almost all extracted.	About one-half extracted.	Very little extracted	Very little extracted
Acid Violet 4 R	507	Less than one-half extracted.				do	do	Larger part extracted.	Little extracted.	Little extracted
Fast Brown	139	do				do	Larger part extracted.	do	Nearly all precipitated.	[illegible]
Resorcin Yellow	84	do				do	do	do	Little extracted.	[illegible]
Crocein Scarlet 8 B	169	About one-half extracted.				do	do	do	Larger part extracted.	[illegible]
New Red L	163	About one-half extracted and precipitated.				do	do	do	Almost all precipitated.	[illegible]
Cotton Scarlet	146	About one-half extracted.				do	do	do	Larger part extracted.	[illegible]
Quinolin Yellow	667									
Fast Brown [illegible]	[illegible]	More than one-half extracted				Almost all extracted.	Almost all extracted.	Larger part extracted.	Larger part extracted.	Larger part extracted.
Azo [illegible]	[illegible]	Almost all extracted.				do	do	do	do	Some extracted; much precipitated.
[illegible]	540	More than one-half extracted, some precipitated.				do	do	do	Almost all extracted.	Larger part extracted.
Eosin B	[illegible]	Some extracted; much precipitated.				Almost all extracted and precipitated.	Almost all extracted and precipitated.	do	Some extracted; much precipitated.	Some extracted; much precipitated.
Eosin [illegible]		do				do	do	do	do	[illegible]
Orange I	85	Almost all extracted.						do		Larger part extracted.
Orange II	56	do						do		Almost all extracted.
Brilliant Orange R	54	do						do		
Crocein Orange	13	do						do		
Orange R	97	do						do		
[illegible]	329	do						do		
Metanil Yellow	95	do						do		
Orange IV	88	do						do		
Fast Brown	101	do						do		
Azo [illegible]	92	do								
Fast Red A	102	do								
[illegible]	510	Less than one-half extracted.								
Rosolic Acid	483	Almost all extracted.								
Meta Chrome Orange	26	do								
Chrysamin G	220	do								
Chrysamin R	269	do								
[illegible] G	10	do								
Eosin	512	Larger part extracted.								
Saffrosin	515	do								
Erythrosin G	516	do								
Victoria Yellow	2	do								

FROM AQUEOUS SOLUTIONS BY IMMISCIBLE SOLVENTS.

ll cases refer to the amount of dye taken up by the organic solvent.)

DICHLORHYDRIN AND SODIUM CHLORID SOLUTION			ANILIN AND ACID (ANILIN HYDROCHLORID 5 PER CENT SODIUM CHLORID SOLUTION)			DICHLORHYDRIN-CARBON TETRACHLORID MIXTURE (EQUAL VOLUMES) AND 1/4 NORMAL HYDROCHLORIC ACID	S-NORMAL SULPHURIC ACID AND AMYL ALCOHOL-GASOLINE MIXTURE (EQUAL VOLUMES)	AMYL ALCOHOL (NORMAL) AND 5 PER CENT SODIUM CARBONATE SOLUTION	S. & J. No.	COLOR
5 per cent sodium chlorid	20 per cent sodium chlorid	[illegible]	[illegible]	[illegible]	1/64 Normal					
	Little extracted								...	Caramel
									462	Acid Magenta
er part extracted	Almost all extracted								435	Light Green S F yellowish
do	do								434	Light Green S F bluish
do	do								430	Cyanole extra
do	do								491	Wool Green S
ost all extracted.	do					More [illegible] extracted			433	Patent Blue
do	do								602	Nigrosin
e extracted.	None extracted.								108	Ponceau 6 R
little extracted.	Very little extracted.		Almost all extracted				Little extracted		8	Acid Yellow G
									9	Acid Yellow R
little extracted.	Very little extracted.		Almost all extracted	Less than one-half extracted			More than one-half extracted		80	Brilliant Yellow S
do	do	Almost all extracted	do	About one-half extracted			Larger part not extracted (three-quarters)		692	Indigo Carmine
do	do								309	Curcumin
extracted.	Not extracted	[illegible]	[illegible]	More [illegible] extracted	[illegible] extracted		Larger part extracted (five-sixths)		107	Amaranth
do	do		do		do		Larger part extracted		106	New Coccin
do	do	[illegible]	Less [illegible] extracted	Little extracted	do		do		91	[illegible]
do	do		Almost all extracted	[illegible]	Little extracted				308	Naphthol Green B
									605	Azo Carmine Bx
									11	Orange G
									188	Naphthol Black B
									20	Chromotrope 2 R
									93	Azo Fuchsin G
									480	Water Blue
AMYL ACETATE AND DILUTE HYDROCHLORIC ACID			ETHER AND DILUTE HYDROCHLORIC ACID							
4 Normal	Normal	1/64 Normal	4 Normal	Normal	1/64 Normal					
little extracted	None extracted.					Very little extracted			54	Palatine Scarlet
do	do					do			55	Ponceau 2 R
do	do					do			56	Ponceau 3 R
							AMYL ALCOHOL AND NORMAL SODIUM HYDROXID			
r part extracted	Less than one-half extracted								4	Naphthol Yellow S
e extracted	Some extracted					Very little extracted			62	Palatine Red
than one half extracted	do					do			64	Crystal Ponceau
o extracted.	do					do			66	Bordeaux B
than one half extracted	do								103	Azo Rubin
e extracted.						Very little extracted			105	Fast Red E
e extracted, much precipitated.	Very little extracted, much precipitated.	Very little extracted							604	Azo Carmine G
little extracted	Very little extracted.	do							600	Rosindulin 2 G
e extracted.	Little extracted.	None extracted							507	Acid Violet 4 R
ly all precipitated.	do								139	Fast Brown
o extracted.	do								84	Resorcin Yellow
er part extracted.	do								169	Croceïn Scarlet 8 B
ost all precipitated.	do								163	New Red L
er part extracted.	do								146	Cotton Scarlet
....									667	Quinolin Yellow
er part extracted.	Larger part extracted								137	Fast Brown
do	Some extracted, much precipitated								287	Azo Blue
ost all extracted	Larger part extracted	Little extracted							516	Alizarin Red S
o extracted; much precipitated.	Some extracted, much precipitated	Some extracted, much precipitated							78	Erika B
do	do	do								Erika G
	Larger part extracted	Little extracted						Larger part not extracted	85	Orange I
	Almost all extracted	do						Almost all extracted	86	Orange II
	do	do							54	Brilliant Orange R
	do	do							13	Croceïn Orange
	do	do							97	Orange R
	do	do							329	Chrysophenin
	do	Larger part extracted	Very little extracted	Less [illegible] extracted	[illegible] extracted				95	Metanil Yellow
	do	do	do	do					88	Orange IV
	do	do	Larger part extracted	Larger part extracted	[illegible] extracted				101	Fast Brown
	do	do	do	do					92	Azo Flavin
	do	do	do	do	do				102	Fast Red A
	do	Almost all extracted	Very little extracted	do	[illegible] all extracted				510	Fluorescein
	do	do	do	Little extracted	do				483	Rosolic Acid
								AMYL ALCOHOL-[illegible] MIXTURE [illegible] AND NORMAL SODIUM HYDROXID		
....			All extracted	All extracted	All extracted		Little extracted	[illegible] extracted	26	Meta Chrome Orange
....			Almost all extracted	Almost all extracted	Almost all extracted		Precipitated	[illegible]cipitated.	220	Chrysamin G
....			do	do	do		do	do	269	Chrysamin R
....			do	All extracted	All extracted		Less than one-half extracted	[illegible] extracted.	10	Sudan G

Orange R		do						do		do
Chrysophenin		do								do
[illegible]		do								do
[illegible]		do								do
Fast Brown		do								do
Azo Flavin		do								do
Fast Red A		Less than one-half extracted								
Fluorescein		Almost all extracted								
[illegible]										
[illegible]		do								
[illegible]		do								
[illegible]		do								
[illegible]		Larger part extracted								
[illegible]		do								
[illegible]		do								
Erythrosin B		do								
Victoria Yellow		More than one-half extracted								
Erythrosin		Larger part extracted								
[illegible]		do								
Rose Bengal		do								
Eosin 10 B		do								
Martius Yellow		do								
[illegible]		Almost all extracted								
Fast Bordeaux		do								
[illegible]		More than one-half extracted	More than one-half extracted	More than one-half extracted	About one-half extracted					Very little extracted.
[illegible]		Less than one-half extracted	About one-half extracted	About one-half extracted.	do					Little extracted.
Persian Berries		Larger part extracted								More than one-half extracted.
Quercitron Bark		Almost all extracted								Almost all extracted.
Fustic		do								do
Logwood		Very little extracted				Almost all extracted.	Almost all extracted	Almost all extracted.		Little extracted.
Cochineal		Almost all extracted and precipitated								Larger part extracted and precipitated
Archil										
Cudbear		do								Larger part extracted.
[illegible]		do								Almost all extracted.
[illegible]		do								do
Congo Red		Almost all extracted	Precipitated	Precipitated.	Precipitated.	Precipitated.	Precipitated.			Precipitated.
Formyl Violet S 4 B		do	Very little extracted	Very little extracted	Little extracted.	Larger part extracted.	Almost all extracted.	Almost all extracted.		None extracted.
Acid Violet		do	do	Little extracted	Larger part extracted.	do	do	do		do
Methyl Alkali Blue		do	All extracted	All extracted	All extracted.	All extracted.	All extracted.	All extracted.		None extracted, but precipitated
Guinea Green B		do	About one-half extracted	About one-half extracted	About one-half extracted.	More than one-half extracted.	More than one-half extracted.	More than one-half extracted.		None extracted.
Brilliant Milling Green			Larger part extracted	Larger part extracted	Almost all extracted.	Almost all extracted.	Almost all extracted.	Almost all extracted.		do
							ETHER AND SODIUM HYDROXID SOLUTIONS			
							Normal	1/4 Normal	1/16 Normal	1/64 Normal
Thio Flavin T			Little extracted	Less than one-half extracted	About one-half extracted.		Very little extracted.			
Methylene Blue			Larger part not extracted	do	Larger part extracted.		Little extracted.			
[illegible]			Larger part extracted	Larger part extracted.	do		Less than one-half extracted.	Less than one-half extracted.	Less than one-half extracted.	
[illegible]		[illegible]	do	do	do		Little extracted.	Little extracted.	Little extracted.	
[illegible]			do		Almost all extracted.		Larger part extracted.	More than one-half extracted.	Less than one-half extracted.	Little extracted.
[illegible]			Almost all extracted		do		Almost all extracted.	Larger part extracted.	About one-half extracted.	Less than one-half extracted.
Magenta			Very little extracted		Little extracted.		Larger part extracted.			
Malachite Green B			Less than one-half extracted		Less than one-half extracted.		do			
Malachite Green G							do			
Methyl Violet					Less than one-half extracted		do			
Crystal Violet					About one-half extracted		do			
Iosamin G			[illegible]		Almost all extracted		Almost all extracted.	Larger part extracted	Larger part extracted.	Larger part extracted.
Auramin O			[illegible]		Larger part extracted		do	Almost all extracted	Almost all extracted.	Almost all extracted.
Acridin G							do			
New Methylene Blue			[illegible]		Almost all extracted.		do	Almost all extracted.	Almost all extracted.	Almost all extracted.
Bismarck Brown			[illegible]		Less than one-half extracted		do	do	do	do
Bismarck Brown R		[illegible]			do		do	do	do	do
Chrysoidin Y	1	do	[illegible]		Almost all extracted.		do	do	do	do
Chrysoidin R	18	do			Larger part extracted.		do	do	do	do
Rhodamin B	504	do			Almost all extracted		do	do	do	do
Rhodamin G	502	do			do		do	do	do	do
Butter Yellow	10									
Anilin Yellow										
o-Amidoazotoluene										
Benzene-azo-α-naphthylamin										
Yellow A B										
Yellow O B										
α-Amidoazonaphthalene										
Quinolin Yellow S. L.	[illegible]									
Benzene-azo-α-naphthol							Larger part extracted.			
β-naphthalene-azo-α-naphthol							Larger part not extracted	Larger part not extracted		
Sudan Brown							Larger part extracted.	Larger part extracted	Almost all extracted.	All extracted.
Sudan I	11						Almost all extracted.	All extracted.	All extracted.	do
Sudan II	40									
Carminaph Garnet	[illegible]									
Sudan III	143									

[1] None extracted in ether and sodium hydroxid solutions.
[2] Almost all extracted in dichlorhydrin and sodium chlorid solutions (5 and 25 per cent sodium chlorid) neutral

do		do							75	Erika B
	Larger part extracted.	Little extracted.				Almost all extracted.				Erika G
	Almost all extracted.	do						Larger part not extracted	85	Orange I
	do	do						Almost all extracted	86	Orange II
	do	do						do	54	Brilliant Orange R
	do	do						do	13	Crocein Orange
	do	do						do	97	Orange R
	do	Larger part extracted.	Very little extracted.	Less than one-half extracted.	Little extracted.			do	329	Chrysophenin
	do	do	do	do	do			do	95	Metanil Yellow
	do	do	Larger part extracted.	Larger part extracted.	Little extracted.			do	88	Orange IV
	do	do	do	do	do			do	101	Fast Brown
	do	do	do	do	do			do	92	Azo Flavin
	do	Almost all extracted.	Very little extracted.	do	Almost all extracted.			do	102	Fast Red A
	do	do	do	Little extracted.	do				510	Fluorescein
									483	Rosolic Acid
								AMYL ALCOHOL-GASOLINE MIXTURE (3:1) AND NORMAL SODIUM HYDROXID		
			All extracted.	All extracted.	All extracted.		Little extracted.	Not extracted.	26	Meta Chrome Orange
			Almost all extracted.	Almost all extracted.	Almost all extracted.		Precipitated.	Precipitated.	220	Chrysamin G
			do	do	do		do	do	269	Chrysamin R
			do	All extracted.	All extracted.		Less than one-half extracted.	Little extracted.	10	[illegible]
			do	Almost all extracted.	Almost all extracted.		do	Very little extracted.	512	Eosin
			do	do	do		Larger part not extracted.	do	515	Safrosin
			do	do	do		Less than one-half extracted.	do	516	Erythrosin G
			do	do	do		About one-half extracted.	Less than one-half extracted.	2	Victoria Yellow
					About one-half extracted.				1	Picric Acid
			Almost all extracted.	Almost all extracted.	Almost all extracted.		Larger part extracted.	Less than one-half extracted.	517	Erythrin
			do	do	do		do	do	518	Phloxin
			do	do	do		do	About one-half extracted.	52[illegible]	Rose Bengal
			do	do	do		Almost all extracted.	More than one-half extracted.	521	Eosin 10 B
			do	do	do		do	Almost all extracted.	3	Martius Yellow
			do	do	do				6	Aurantia
			do	do	do		Almost all extracted	Almost all extracted.	524	Rose Bengal
	Very little extracted.	Very little extracted.	Very little extracted.	Very little extracted.	Very little extracted.					Saffron
	Little extracted.	Little extracted.	do	do	do				700	Persian Berries
	More than one-half extracted.	More than one-half extracted.	Larger part not extracted.	Larger part not extracted.	Larger part not extracted.				699	Quercitron Bark
	Almost all extracted.	Almost all extracted.	Almost all extracted.	Almost all extracted.	Almost all extracted.				698	Fustic
	do	Larger part extracted.	Very little extracted.	Very little extracted.	Very little extracted.				702	Logwood
	Little extracted.	Little extracted.	do	do	do				706	Cochineal
	Larger part extracted and precipitated	Larger part extracted and some precipitated.	Little extracted.	Little extracted.	Little extracted.				710	Archil
	Larger part extracted.	Larger part extracted.	Larger part extracted.	Larger part extracted.	Larger part extracted.					Gamboge
	Almost all extracted.	Almost all extracted.	Almost all extracted.	Almost all extracted.	Almost all extracted.				707	Turmeric
	do	do	do	do	do				709	Annatto
	Precipitated.								240	Congo Red
	None extracted.					Almost all extracted.			468	Formyl Violet S4B
	do					do			464	Acid Violet N
	None extracted, but precipitated.					do			476	Methyl [illegible]
	None extracted.					do			441	Guinea Green B
	do					do			438	Brilliant M[illegible]
R AND SODIUM HYDROXID SOLUTIONS								ETHER AND NORMAL ACETIC ACID		
1/16 Normal	1/64 Normal	1/256 Normal								
						Larger part extracted.			658	Thio Flavin T
						do			650	Methylene [illegible]
than one-half extracted.						Almost all extracted.			639	Meldola's B[illegible]
le extracted.									496	Rhodamin S
than one-half extracted.	Little extracted.	Little extracted.							584	Safranin
ut one-half extracted.	Less than one-half extracted.	do							5[illegible]5	Rhodamin 6 G
									448	Magenta
									42[illegible]	Malachite Green B
									428	Malachite Green G
									451	Methyl Violet
									452	Crystal Violet
er part extracted.	Larger part extracted.	About one-half extracted.							499	Irisamin G
ost all extracted.	Almost all extracted.	Almost all extracted.							425	Auramin O
									426	Auramin G
ost all extracted.	Almost all extracted.	Almost all extracted.							655	New Methylene Blue
do	do	do							197	Bismarck Brown
do	do	do							201	Bismarck Brown R
do	do	do							17	Chrysoidin Y
do	do	do						Larger part not extracted.	18	Chrysoidin R
do	do	Larger part extracted.						do	504	Rhodamin B
do	do	do						do	502	Rhodamin G
			Very little extracted.		Almost all extracted.			All extracted.	16	Butter Yellow
			do		do			do	7	Anilin Yellow
			Less than one-half extracted.	Almost all extracted.	Almost all extracted.			do		o-Amino-azo-toluene
			Very little extracted.					do		Benzene-azo-α-naphthylamin
			Much extracted.	Almost all extracted.	All extracted.			do		Yellow A B
			do	do	do			do		Yellow O B
			do	do	do			do		α-Amino-azo-naphthalin
			Almost all extracted.	All extracted.				do	666	Quinolin Yellow S. L
		Larger part extracted.	do	do				do		Benzene-azo-α-naphthol
ost all extracted.	All extracted.	All extracted.						do		B-naphthalene-azo-α-naphthol
xtracted.	do	do						do	59	Sudan Brown
								do	11	Sudan I
								do	49	Sudan II
								do	60	Carminaph Garnet
								do	143	Sudan III

Mixtures of dyes of practically identical solubility can in most cases be separated satisfactorily by chemical means or by precipitation reactions. As the fractionation will have removed all except the few dyes belonging to a known group, suitable chemical methods may usually be chosen without difficulty.

Since both basic and acid triphenylmethane colors tend to undergo slow intermolecular changes when treated with acids and alkalies (adjustment of equilibrium between carbinol, imid and ammonium forms) their complete separation by means of solvents is less simple than that of most other classes.

It will be noticed that ether, amyl acetate and amyl alcohol show corresponding properties as solvents except that the colors are more soluble in amyl acetate than in ether and very much more soluble in amyl alcohol than in the others. Dichlorhydrin is intermediate between amyl alcohol and amyl acetate as regards the sulphonated oxy-azo dyes. For the triphenylmethane colors—it is a much more powerful solvent than amyl alcohol.

REACTIONS OF INDIVIDUAL COLORING MATTERS.

The chemical tests preferred by different analysts will not be the same, but unquestionably those whose chemistry is well understood and that may be considered reactions of certain groups, will be found most useful. Two tests of this type adapted for use with the small amounts of dyes obtained from food products and perhaps not very generally applied at present are those with bromin-hydrazin sulphate and with ammonium cyanid and they have been studied in some detail by the associate referee. Further, in connection with the use of nitrous acid in identifying small amounts of amino compounds hydrazin sulphate has been found to be a suitable reagent for the removal of the excess of nitrous acid, making the test in nearly all cases more convenient and reliable. The diazo compound of Safranin, however, reacts with hydrazin sulphate, apparently.

Most widely employed of the common tests for coloring matters are perhaps the color changes produced by reagents on the dyed fiber. A special effort has been made to gather together the best data concerning these. Loomis, in Bureau of Chemistry Circular 63, gives the reactions of a large number of coloring matters when dyed on wool, or for the oil soluble colors, on silk. These observations were made with dyes of established identity and in this laboratory the statements in the literature have also been checked for some 35 colors with preparations made from pure materials.

These general tests, namely, the reactions of the dyes with acids and alkalies, with bromin and hydrazin sulphate, with nitrous acid and

finally, the more easily carried out of the well-known reactions involving reduction, have been collected in a set of tables, the dyes being arranged in the order of their solubilities. The properties of the different members of a group with similar solubilities may thus be at once compared and suitable reactions for their separation selected.

These tables because of their length are not included in this report, but it is hoped that they may be brought before the collaborators next year for further elaboration and criticism and perhaps may serve as a nucleus for a logical, coherent chapter on food colors to be incorporated in the official methods.

RECOMMENDATION.

It is recommended by the associate referee that work bearing on the separation and identification of the common food coloring matters be continued.

REPORT ON FRUIT PRODUCTS.

By H. C. Gore, *Associate Referee.*

The work planned by the associate referee on fruit products for 1913 consisted in developing further certain studies on the effect of uranyl acetate on the polarization of malic and tartaric acids, and in the application of a procedure due to Yoder for the estimation of malic and tartaric acids in various fruit products. In the last study it was expected that coöperative work would be used to determine the value of the method. After the studies on the effect of uranyl acetate had been made, however, the effect of another reagent, ammonium molybdate, on the polarizations of the two acids was studied, and the effect of the respective reagents on the polarization of lactic acid. Time has been lacking for the trials planned of the Yoder procedure. This, therefore, remains as a subject for further work.

EFFECT OF VARYING AMOUNTS OF URANYL ACETATE ON THE POLARIZATIONS OF MALIC AND TARTARIC ACIDS.

The effect of increasing amounts of uranyl acetate on the polarization of malic and tartaric acids respectively, both free and neutralized, when the concentration of the organic acid was at 1 gram in 100 cc. of solution as polarized, was shown in the 1912 report on fruit products. The study has been carried further, working with more dilute solutions. The data are given in the Table 1. Merck's c. p. malic acid and Mallinckrodt's c. p. tartaric acid were used.

All the solutions of malic and tartaric acid were freshly prepared and read in the polariscope at 20°C. The readings were made in 200 mm.

tubes, using white light from an incandescent carbon filament. The sample of uranyl acetate used was the same used in the studies reported in the 1912 report. It contained 55.475 per cent of uranium. Each gram of malic or tartaric acid thus required 3.2090 grams and 2.8665 grams respectively for one molecular equivalent.

Where large amounts of uranyl acetate were present the optical dispersion was marked. The necessity of using the bichromate cell to obtain more correct readings was not realized and the readings are therefore slightly less certain than if the cell had been used.

The concentration stated is that of malic or tartaric acid in the solution polarized.

TABLE 1.

Effect of uranyl acetate on the polarization of malic and tartaric acids.

ACID AND CONCENTRATION	URANYL ACETATE USED		FREE ACID		NEUTRALIZED ACID	
	Molecular equivalents	Grams per 100 cc.	Polarization	Specific rotatory power	Polarization	Specific rotatory power
			°V.	°V.	°V.	°V.
Malic acid:						
0.1 gram in 100 cc.....	$\frac{1}{4}$	0.080	− 0.30	− 52	− 0.65	−113
	$\frac{1}{2}$	0.160	− 0.90	−156	− 1.40	−243
	$\frac{3}{4}$	0.241	− 1.45	−252	− 2.10	−364
	1	0.321	− 1.90	−330	− 2.80	−486
	$1\frac{1}{4}$	0.401	− 2.30	−399	− 2.80	−486
	$1\frac{1}{2}$	0.481	− 2.55	−442	− 2.80	−486
	$1\frac{3}{4}$	0.562	− 2.75	−477	− 2.70	−468
	2	0.641	− 2.75	−477	− 2.70	−468
	$3\frac{1}{2}$	1.123	− 2.65	−460	− 2.60	−451
	5	1.605	− 2.65	−460	− 2.60	−451
0.2 gram in 100 cc.....	$\frac{1}{4}$	0.160	− 0.85	− 74	− 1.35	−117
	$\frac{1}{2}$	0.321	− 1.95	−169	− 2.95	−256
	$\frac{3}{4}$	0.481	− 2.95	−256	− 4.45	−386
	1	0.642	− 3.80	−330	− 5.80	−503
	$1\frac{1}{4}$	0.802	− 4.70	−408	− 5.90	−512
	$1\frac{1}{2}$	0.962	− 5.35	−464	− 5.70	−494
	$1\frac{3}{4}$	1.123	− 5.65	−490	− 5.60	−486
	2	1.284	− 5.65	−490	− 5.50	−477
	$3\frac{1}{2}$	2.246	− 5.35	−464	− 5.40	−468
	5	3.209	− 5.30	−460	− 5.40	−468
0.5 gram in 100 cc.....	$\frac{1}{4}$	0.401	− 2.30	− 80	− 3.90	−135
	$\frac{1}{2}$	0.802	− 4.70	−163	− 7.45	−258
	$\frac{3}{4}$	1.203	− 7.10	−246	−11.30	−392
	1	1.605	− 9.50	−330	−14.70	−510
	$1\frac{1}{4}$	2.006	−11.70	−406	−14.55	−505
	$1\frac{1}{2}$	2.404	−13.45	−467	−14.40	−500
	$1\frac{3}{4}$	2.808	−14.30	−496	−14.25	−494
	2	3.209	−14.20	−493	−14.00	−486
	3	4.814	−13.85	−481	−13.75	−477
Tartaric acid:						
0.1 gram in 100 cc.....	$\frac{1}{4}$	0.072	0.55	95	0.90	156
	$\frac{1}{2}$	0.143	1.10	191	1.55	269
	$\frac{3}{4}$	0.215	1.40	243	2.20	382
	1	0.286	1.70	295	2.50	434
	$1\frac{1}{4}$	0.358	2.20	382	2.50	434

TABLE 1—Continued.

ACID AND CONCENTRATION	URANYL ACETATE USED		FREE ACID		NEUTRALIZED ACID	
	Molecular equivalents	Grams per 100 cc.	Polarization	Specific rotatory power	Polarization	Specific rotatory power
			°V.	°V.	°V.	°V.
Tartaric acid—*Con.*:						
0.1 gram in 100 cc.....	1½	0.430	2.40	416	2.15	373
	1¾	0.502	2.45	425	2.00	347
	2	0.573	2.20	382	1.85	321
	3½	1.003	1.30	226	0.95	165
	5	1.433	(?)0.90	156	0.75	130
0.2 gram in 100 cc.....	¼	0.143	1.15	100	1.85	160
	½	0.286	1.95	169	3.10	269
	¾	0.430	2.80	243	4.35	377
	1	0.563	3.45	299	5.30	460
	1¼	0.717	4.30	373	4.90	425
	1½	0.860	4.65	403	4.60	399
	1¾	1.003	4.85	421	4.20	364
	2	1.146	4.55	395	3.85	334
	3½	2.007	2.85	247	2.35	204
	5	2.866	1.95	169	1.80	156
0.5 gram in 100 cc.....	¼	0.358	2.10	73	4.50	156
	½	0.717	4.20	146	7.65	265
	¾	1.075	6.35	220	10.65	370
	1	1.433	8.40	291	12.90	448
	1¼	1.791	10.10	350	12.45	432
	1½	2.150	11.40	395	11.65	404
	1¾	2.508	11.90	413	10.95	380
	2	2.866	11.20	389	10.30	357
	3	4.300	8.75	304	8.10	281

As in the work reported in 1912 it is here found that when neutralized malic or tartaric acid was employed, maximum values were reached in the presence of smaller amounts of uranyl acetate and the polarizations were higher, than when the free acids were used. Excessive amounts of uranyl acetate caused marked depressions of the polarizations. As before, such depressions were most marked in solutions containing tartaric acid. They were especially large at low concentrations of tartaric acid; for example, the specific rotatory power gradually changed from 434 to 130 in a solution containing 0.1 gram in 100 cc. of neutralized tartaric acid, when the uranyl salt was increased from 1 to 5 molecular equivalents.

In the work reported in 1912 it was found that in case of malic acid, concentration 1 gram in 100 cc., depressions in readings caused by excessive amounts of uranyl acetate could be overcome by adding suitable amounts of acetic acid, the fact having been first observed by Yoder. With tartaric acid such depressions could be but partly overcome in this way. The observations recorded in the table below show that the same facts hold at lower concentrations of the respective acids.

TABLE 2.

Effect of acetic acid with uranyl acetate on the polarization of malic and tartaric acids.

ACETIC ACID PRESENT	POLARIZATIONS	
	Neutralized malic acid	Neutralized tartaric acid
cc.		
0.0	−5.35	+2.30
0.1	−5.45	+2.55
0.2	−5.35	+3.00
0.4	−5.45	+3.50
1.0	−5.80	+4.40
2.0	−5.85	+4.50
3.0	−5.65	+4.45
4.0	−5.35	+4.30

The polarizations were made of solutions containing in addition to neutralized malic or tartaric acid, $3\frac{1}{2}$ molecular equivalents of uranyl acetate, and amounts of acetic acid ranging from 0 to 4 cc. per 100 cc. of solution. The concentration of each solution polarized was 0.2 gram per 100 cc. of malic or tartaric acid.

As the polarizations of solutions containing the same amounts of neutralized malic or tartaric acid, and sufficient uranyl acetate ($1\frac{1}{4}$ and 1 molecular equivalent respectively) to give maximum readings are − 5.90 (malic) and + 5.30 (tartaric), the maximum polarization of the solution of malic is shown to be almost entirely restored (from − 5.35 up to − 5.85) by addition of correct amounts of acetic acid, while the polarization of the solution of tartaric acid was but partially restored (from + 2.30 to + 4.50).

EFFECT OF AMMONIUM MOLYBDATE ON THE POLARIZATION OF MALIC AND TARTARIC ACIDS.

A limitation of the uranyl acetate method proposed by Dunbar and Bacon[1] for the estimation of malic acid is that it fails in the presence of tartaric acid. Yoder[2] pointed out that if the sum of the two acids, malic and tartaric, is known, the respective amounts of each may be calculated from the increases in polarization upon addition of uranyl acetate. In a natural product, however, the sum of the two acids is never known with exactness owing to the presence of other acids, acid salts, phosphates and amphoteric amido bodies. Dunbar[3] has proposed as a measure of the two acids present the amount of oxalic acid formed upon oxidation with alkaline permanganate of the mixture of acids first separated as lead salts.

[1] Bur. Chem. Cir. 76.
[2] *J. Ind. Eng. Chem.*, 1911, **3**: 563; *Zts. Nahr. Genussm.*, 1911, **22**: 329.
[3] Bur. Chem. Cir. 105 and 106.

The method while of promise under certain conditions is not applicable when citric acid or some other substance is present which is precipitated as lead salt and gives oxalic acid on oxidation. If another equation relating to the quantities of malic and tartaric acid present could be found to supplement the equation proposed by Yoder expressing the combined polarizations with uranyl salts, it seemed probable that both acids could be determined by optical methods alone; the literature was therefore searched for an account of another element which would cause changes in the optical rotation of malic and tartaric acids.

Of the many salts which are described in the literature as affecting the optical rotation of these acids, ammonium molybdate appeared to be of most promise. Gernez[1] published an extended series of papers dealing with the effect of salts of molybdic and tungstic acids on the polarization of malic and tartaric acids, and on certain optically-active higher alcohols. For malic acid and ammonium molybdate Gernez found a maximum positive reading of $(A)_D = +740$. This is in marked contrast to the maximum reading of $(A)_D = -501$ found by Yoder[2] for uranyl acetate and malic acid,—a difference of 1241 degrees.

Richardson and Gregory[3] used ammonium molybdate in the study of the estimation of tartaric acid and tartrates. The relation between the polarizations and amounts of tartaric acid present was found not to be linear, but the polarizations very rapidly increased until at the higher concentrations a specific rotatory power of 861.8° was reached.

Rimbach and Schneider[4] studied the effect of ammonium molybdate and other salts of molybdenum, also tungsten, uranyl, titanium, zirconium, and other elements on the polarization of quinic acid. The extremely high polarizations caused by ammonium molybdate with malic and tartaric acids were not found in their study.

Rosenheim and Itzig[5] studied the compounds of beryllium with malic and tartaric acids, and with substituted derivatives of succinic acid. Crystalline d-beryllium tartrates were prepared of high specific rotatory powers. Upon dilution remarkable stability was shown by the fact that the high specific rotatory powers persisted. Tentative structural formulae were suggested.

Itzig[6] later studied the effects of salts of molybdenum and other metals on the polarization of tartaric acid and many of its salts and upon malic acid, without, however, having in mind the estimation of the respective acids. Data similar in many respects to facts described by Gernez were obtained.

[1] Gernez papers in *Compt. rend.*, 1887 to 1890 incl.
[2] Loc. cit.
[3] *J. Soc. Chem. Ind.*, 1903, **22**: 405.
[4] *Zts. physikal. Chem.*, 1903, **44**: 467.
[5] *Ber. d. Chem. Ges.*, 1899, **32**: 3424; 1900, **33**: 707.
[6] Ibid, 1901, **34**: 1372, 2391, 3822.

The interesting inversions in the polarizations found by Gernez were studied by Grossman and Pötter,[1] and by Maderna[2] as well as other phases of the subject. With the exception of the paper by Richardson and Gregory, in which malic acid was not considered, however, no data has been secured with a view to the development of a method for the estimation of the two acids by use of ammonium molybdate.

PRELIMINARY STUDY.

The ammonium molybdate used contained 54.595 per cent of molybdenum. The calculated percentage of molybdenum is 57.72 for the salt of the formula $(NH_4)_6Mo_7O_{24}$. The deficiency noted was probably due to the presence of water of crystallization. The analysis was made by igniting MoO_3 according to directions given by Treadwell-Hall (*Quantitative Analysis*, Vol. II, p. 250). Each gram of malic and tartaric acid required 1.3123 and 1.1717 grams of the ammonium molybdate respectively for one molecular equivalent of respective acid to one of molybdenum. On account of the high dispersive powers of solutions of ammonium molybdate, the bichromate cell was used throughout. As in the work with uranyl acetate all solutions were made up and read at 20°C. Tubes of 200 mm. length, and white light from an incandescent carbon filament were used.

The effect of increasing amounts of ammonium molybdate on polarizations of solutions of free and neutralized malic and tartaric acids respectively is shown in the following tables. Each solution contained as polarized 1 gram in 100 cc. of one of the acids either free or neutralized.

TABLE 3.

Effect of ammonium molybdate on the polarization of malic and tartaric acids.

ACID AND CONCENTRATION	AMMONIUM MOLYBDATE USED		POLARIZATIONS	
	Molecular equivalents	Grams per 100 cc.	Free	Neutralized
			°V.	°V.
Malic acid:				
1 gram in 100 cc.	0	0.000	....	....
	$\frac{1}{16}$	0.132	− 1.30	− 1.10
	$\frac{1}{4}$	0.328	− 0.65	− 1.55
	$\frac{1}{2}$	0.656	+ 4.95	− 2.10
	$\frac{3}{4}$	0.984	+12.20	− 2.05
	1	1.312	−19.35	− 0.95
	$1\frac{1}{4}$	1.640	+21.35	+ 1.30
	$1\frac{1}{2}$	1.968	+21.40	+ 4.15
	$1\frac{3}{4}$	2.296	+21.10	+ 6.40
	2	2.624	+20.55	+ 7.80
	$3\frac{1}{2}$	4.594	+19.05	+10.50
	5	6.562	+17.80	+10.55

[1]Ibid, 1905, **38**: 3877; *Zts. physikal chem.*, 1906, **56**: 577.
[2]*Atti. R. Accad. dei Lincei, Roma,* 1910 (5) **19** (2): 130.

TABLE 3.—Continued.

ACID AND CONCENTRATION	AMMONIUM MOLYBDATE USED		POLARIZATIONS	
	Molecular equivalents	Grams per 100 cc.	Free	Neutralized
			°V.	°V.
Tartaric acid:				
1 gram in 100 cc.	0	0.000	0.95	2.20
	$\frac{1}{10}$	0.118	3.60	3.70
	$\frac{1}{4}$	0.292	7.20	6.15
	$\frac{1}{2}$	0.586	12.05	9.80
	$\frac{3}{4}$	0.878	15.85	13.40
	1	1.172	19.80	17.25
	$1\frac{1}{4}$	1.464	23.75	21.15
	$1\frac{1}{2}$	1.758	27.30	24.75
	$1\frac{3}{4}$	2.050	30.05	27.45
	2	2.344	31.70	28.15
	$3\frac{1}{2}$	4.100	36.95	29.75
	5	5.856	36.20	30.05

Perhaps the most conspicuous feature of the above table is the peculiar inversion of the curves for free and neutralized malic acid discovered by Gernez. Neutralized malic acid solution was made far less highly active than the solution of the free acid, and the solution of neutralized tartaric acid was made less active than that of free tartaric acid, although the difference is less striking. The questions arise—can these rotations be stimulated by acetic acid, and can conditions be found under which a linear relation exists between concentration of malic or tartaric acid and optical activity?

EFFECT OF ACETIC ACID ON POLARIZATIONS OF SOLUTIONS OF AMMONIUM MOLYBDATE AND NEUTRALIZED MALIC OR TARTARIC ACIDS RESPECTIVELY.

Each of the solutions polarized contained 1 gram in 100 cc. of neutralized malic and tartaric acids respectively, and from 1 to $3\frac{1}{2}$ molecular equivalents of ammonium molybdate. The results are given in Tables 4 and 5.

TABLE 4.

Effect of acetic acid on the polarization of solutions of ammonium molybdate and neutralized malic acid (1 gram in 100 cc).

ACETIC ACID USED	POLARIZATIONS WITH AMMONIUM MOLYBDATE USED			
	1 molecular equivalent (1.312 grams in 100 cc.)	$1\frac{1}{2}$ molecular equivalents (1.968 grams in 100 cc.)	2 molecular equivalents (2.624 grams in 100 cc.)	3 molecular equivalents (3.936 grams in 100 cc.)
cc. in 100 cc.	°V.	°V.	°V.	°V.
0.0	− 0.50	+ 4.55	+ 8.00	+10.20
0.2	+ 3.15	+10.90	+13.95	+15.55
0.4	+ 8.15	+17.95	+26.65	+23.60
1.0	+10.20	+26.55	+38.05	+37.35
2.0	+10.50	+26.90	+41.65	+42.30
4.0	+10.70	+27.30	+42.60	+43.25
6.0	+10.65	+27.05	+42.70	+43.50
10.0	+10.45	+27.20	+42.70	+43.50
16.0	+10.45	+26.95	+42.50	....

TABLE 5.

Effect of acetic acid on the polarization of solutions of ammonium molybdate and neutralized tartaric acid (1 gram in 100 cc.)

ACETIC ACID USED	POLARIZATIONS WITH AMMONIUM MOLYBDATE USED			
	2 molecular equivalents (2.344 grams in 100 cc.)	$2\frac{1}{4}$ molecular equivalents (2.636 grams in 100 cc.)	$2\frac{1}{2}$ molecular equivalents (2.928 grams in 100 cc.)	$3\frac{1}{2}$ molecular equivalents (4.100 grams in 100 cc.)
cc. in 100 cc.	°*V*.	°*V*.	°*V*.	°*V*.
0.0	28.10	28.50	29.00	29.50
0.2	29.45	29.75	30.05	30.30
0.4	30.85	30.90	31.10	31.15
1.0	32.45	33.30	33.20	33.30
2.0	35.20	35.25	35.15	35.10
4.0	36.40	36.20	36.65	37.00
6.0	37.05	37.35	37.35	38.05
10.0	37.50	37.75	38.25	38.70
16.0	37.65	38.20	38.55	.....

In case of malic acid it was expected that maximum readings would be obtained when from 1 to $1\frac{1}{4}$ molecular equivalents of ammonium molybdate had been added and sufficient acetic acid. Instead the readings increased very rapidly with increasing ammonium molybdate, approaching apparently maximum readings when 3 equivalents of the molybdenum salt was present and acetic acid in amounts ranging from 10 to 16 grams in 100 cc.

The results observed in case of tartaric acid are even more unexpected. Regular increases with no indication of approach to maximum readings occurred as ammonium molybdate and acetic acid increased.

SEARCH FOR CONDITIONS IN WHICH THE POLARIZATIONS OF NEUTRALIZED MALIC AND TARTARIC ACIDS MADE ACTIVE BY THE PRESENCE OF AMMONIUM MOLYBDATE AND ACETIC ACID ARE PROPORTIONAL TO THE AMOUNTS OF THE RESPECTIVE ACIDS PRESENT.

Two series of solutions of neutralized malic and tartaric acids containing 2 grams in 100 cc. of the respective acids were prepared, each solution containing 3.5 molecular equivalents of ammonium molybdate. Each series consisted of six solutions in which the amounts of acetic acid present varied from 0 to 20 cc. in 100 cc. Portions of each solution were diluted to concentrations of 2, 1, 0.5, 0.4, and 0.2 gram of optically active acid in 100 cc., and readings were made on all solutions in the polariscope. The readings are given in Table 6.

TABLE 6.

Polarizations of fixed solutions of neutralized malic and tartaric acids with ammonium molybdate and acetic acid.

CONCENTRATION OF MALIC OR TARTARIC ACID	ACETIC ACID PRESENT	NEUTRALIZED MALIC ACID		NEUTRALIZED TARTARIC ACID	
		Polarization	Specific rotatory power	Polarization	Specific rotatory power
grams in 100 cc.	*cc. in 100 cc.*	*°V.*	*°V.*	*°V.*	*°V.*
2.0	0.0	10.55	92	60.70	526
2.0	4.0	85.25	739	71.70	622
2.0	6.0	86.25	748	74.80	649
2.0	8.0	86.90	754	77.00	668
2.0	10.0	87.25	757	78.85	684
2.0	20.0	87.00	754	86.00	746
1.0	0.0	10.80	187	29.55	513
1.0	2.0	42.20	732	35.30	612
1.0	3.0	42.90	744	36.20	628
1.0	4.0	43.10	748	36.90	640
1.0	5.0	43.30	751	37.40	649
1.0	10.0	43.35	752	38.45	667
0.5	0.0	8.20	284	14.20	493
0.5	1.0	20.55	713	16.50	572
0.5	1.5	21.05	730	16.75	581
0.5	2.0	21.25	737	16.75	581
0.5	2.5	21.20	735	16.75	581
0.5	5.0	21.30	739	16.60	576
0.4	0.0	7.25	314	11.00	477
0.4	0.8	16.25	705	12.85	557
0.4	1.2	16.75	726	12.85	557
0.4	1.6	16.80	729	13.05	566
0.4	2.0	16.85	731	13.00	564
0.4	4.0	16.95	735	12.80	555
0.2	0.0	4.15	360	5.25	455
0.2	0.4	7.80	676	5.50	477
0.2	0.6	8.10	702	5.35	464
0.2	0.8	8.15	707	5.35	464
0.2	1.0	8.05	698	5.35	464
0.2	2.0	8.40	728	5.15	446

The results show that the rotation of malic acid stimulated to or near the maximum point by the presence of suitable amounts of ammonium molybdate and acetic acid, are practically proportional to the concentration of malic acid. With tartaric acid this is not the case, but the specific rotatory power falls with increasing concentration indicating dissociation with dilution of the highly rotating complex of molybdenum and tartaric acid. It was hoped that conditions of strictly linear relations would exist between the increases in polarization and amounts of respective acids present. If this were the case the estimation of malic and tartaric acids in the presence of each other could be easily made by determining the increases in polarization after the addition of uranyl acetate and ammonium molybdate respectively. As, however, such relations were not found, it remains for tables to be constructed from data yet to be worked out from which may be read the amounts of malic or tartaric acid corresponding to a deter-

mined change in optical rotation. No method for the estimation of the two acids in the presence of each other by polarimetric means alone is in sight at present.

STUDY OF THE EFFECT OF URANYL ACETATE AND AMMONIUM MOLYBDATE ON THE POLARIZATION OF LACTIC ACID.

In the report of 1912 it was shown that the presence of sucrose and invert sugar did not interfere perceptibly with increases in optical activity when uranyl acetate was added to solutions containing malic acid. Two substances, however, exist widely distributed in nature, one of which, mannite, is known to be made very active in optical rotation by uranyl salt (Grossman)[1] and by ammonium molybdate (Gernez)[2] and the other, lactic acid, might, it was thought, interfere as it is optically active and possesses the carboxy grouping present in both malic and tartaric acids. Tests were therefore made to determine the extent to which polarizations of lactic acid are made active, by uranyl acetate and ammonium molybdate. It may be stated here, however, that as by precipitation as barium salt by the Yoder procedure the sample is freed from possible presence of mannite or lactic acid and studies of the effects of the reagents on the polarizations of these substances are without interest where this method is used. They are of importance however, in connection with short methods like that of Dunbar and Bacon.

The sample of high grade commercial lactic acid used polarized directly at 20°C. in a 200 mm. tube at 20°C. at + 16.4°V. Titration showed that the sample contained 88.2 per cent of total lactic acid, of which about 20 per cent was present as lactid. For the polarimetric study 20 grams of the sirupy acid was diluted, treated with a slight excess of solutions of sodium hydroxid, heated to boiling, and boiled for a few minutes. It was then acidified with hydrochloric acid, then made just alkaline, and the boiling continued. The pink color of the phenolphthalein remained unchanged in intensity. It was therefore concluded that all the lactic had been converted into the sodium salt of lactic acid. The solution was now cooled, exactly neutralized and made up to 100 cc. The solution polarized at + 3.00°V. = $(A)_D$ = + 2.95.

Of this solution portions of 5 cc. were treated with slightly more than one molecular equivalent of uranyl acetate and ammonium molybdate respectively, diluted to 100 cc. and polarized.

The polarizations were as follows:

Uranyl acetate	−0.6°V., $(A)_D$ = −11.8
Ammonium molybdate	+0.5°V., $(A)_D$ = + 9.8

[1] *Zts. Ver. d. Zucker-Ind.*, n.f., 1905, **42**: 1058.
[2] Loc. cit.

Thus, though uranyl acetate and lactic acid polarized to the left, and ammonium molybdate and lactic acid polarized to the right, the changes are quite small. Further tests showed that these polarizations were not increased by adding acetic acid.

SUMMARY.

Studies were made on the effect of increasing amounts of uranyl acetate on the polarizations of malic and tartaric acids respectively when the acids were present in concentrations of 0.1, 0.2, and 0.5 gram per 100 cc. As previously found with concentrations of 1 gram in 100 cc. excessive amounts of the reagent caused depressions in optical activity particularly marked in case of tartaric acid. By adding suitable amounts of acetic acid the maximum activity was almost entirely restored in case of malic acid, but only partly restored in case of tartaric.

Studies on the effect of ammonium molybdate on the optical rotation of malic and tartaric acids showed the known great magnification of the rotations, and showed great differences in optical activity depending on whether the particular acid was free or neutralized. Acetic acid added to solutions containing neutralized malic or tartaric acid greatly increased the optical activities. With malic acid, in the presence of suitable amounts of ammonium molybdate and acetic acid, very large positive polarizations were obtained which were practically proportional to the amounts of malic acid present. With tartaric acid very large positive polarizations were obtained in the same manner, but the readings were not proportional to the amounts of tartaric acid present.

The polarizations of lactic acid were found to be so slightly affected by either uranyl acetate or ammonium molybdate that it could hardly interfere, if present, in solutions being polarized.

RECOMMENDATIONS.

It is recommended that the study of the effects of uranyl acetate and ammonium molybdate respectively, on the polarizations of malic and tartaric acids, in the presence of known amounts of acetic acid, be continued, with the view of constructing tables from which the amounts of malic or tartaric acid present can be read, when the change in optical rotation due to either reagent is known.

That the Yoder procedure for the estimation of malic and tartaric acids be studied in connection with such tables.

Two papers giving the results of preliminary work on "Determination of Total Solids in Fruit Juices and on Fruit Jellies and their Manufacture" were read by L. W. Andrews.

REPORT ON WINE.

By B. G. Hartmann, *Associate Referee.*

This year's work on wine was devoted to the determination of tartaric acid. As was pointed out in the Proceedings of 1912, the customary method of determining tartaric acid, as described in Bulletin 107, Revised, does not give satisfactory results when applied to wines containing considerable amounts of free tartaric acid. It was decided, therefore, to try out the modification of this method as outlined by Hartmann and Eoff (Bur. Chem. Bul. 162, p. 71) with a view of ascertaining how this method compares with the bulletin method, and of determining its reliability in the hands of different analysts.

Accordingly, two California white wines were sent to six collaborators. No 1 was a straight wine and No. 2 was the same wine to which 300 mg. of tartaric acid per 100 cc. were added.

DIRECTIONS TO COLLABORATORS.

1. Mix the contents of the quart and pint bottles of each set and filter.
2. Transfer 20 cc. of the filtered wine to a 400 cc. beaker and bring to an incipient boil to drive out carbonic acid. Add 20 cc. of recently-boiled distilled water and titrate with tenth-normal sodium hydroxid solution using phenolphthalein as indicator.

DETERMINATION OF TARTARIC ACID.

Bulletin method.—Follow the directions given on page 86 of Bulletin 107, Revised, using phenolphthalein as an inside indicator instead of litmus paper in the titration of tartaric acid.

Hartmann and Eoff method modified.—Measure 50 cc. of filtered wine into a 250 cc. beaker and completely neutralize with normal sodium hydroxid. (The amount of sodium hydroxid necessary to accomplish this is found by multiplying by 0.25 the number of cubic centimeters of tenth-normal sodium hydroxid required to neutralize the 20 cc. of wine as determined under 2). To the wine so treated add water to make 100 cc.; add the equivalent of tartaric acid corresponding to the number of cubic centimeters of normal sodium hydroxid added. To find this amount of tartaric acid multiply the number of cubic centimeters of normal sodium hydroxid added by 0.075, which will give the grams of tartaric acid required to convert all the tartaric acid present in the wine into bitartrates. Weigh exactly this amount and dissolve in the 50 cc. of neutralized and diluted wine. Prepare the tartaric acid to be used by pulverizing pure acid and drying for 2 hours in a water oven. Record the weight of tartaric acid added, and after it has gone into solution add 15 grams of potassium chlorid and 2 cc. of glacial acetic acid and stir until the salt is completely dissolved. Add 20 cc. of 95 per cent alcohol and stir one minute; set aside for 15 hours and collect the crop of cream of tartar crystals as directed in the bulletin method and titrate using phenolphthalein instead of litmus paper as indicator.

CALCULATION OF TOTAL TARTARIC ACID.

Bulletin method.—Proceed as described in Bulletin 107, Revised; that is, add 1.5 cc. to burette reading and multiply by 0.015.

Hartmann and Eoff method modified.—Add 1.5 cc. to burette reading and multiply by 0.015. From this amount subtract the tartaric acid added and multiply the difference by 2.

CALCULATION OF FREE TARTARIC ACID AND CREAM OF TARTAR.

In order to figure the free tartaric acid and the cream of tartar, it is necessary to determine the alkalinity of the ash.

Alkalinity of ash.—Measure into a platinum dish 50 cc. of the wine at 20°C., evaporate on a water bath to a sirupy consistency and ash carefully at a dull red heat, never allowing the fumes to ignite. If difficulty is experienced in burning the ash white, leach with hot water. To the white ash add about 5 cc. of water and 3 drops of a 10 per cent solution of ammonium carbonate; evaporate and heat below redness to expel ammonium salts. Add hot water to the ash and transfer the whole to a 7 cm. filter with successive small quantities of hot water until the filtrate amounts to 50 cc. This gives the portion of the ash soluble in water; transfer the portion insoluble in water remaining on the filter to a platinum dish and ash. To the residue add 10 cc. of tenth-normal sulphuric acid and about 10 cc. of water and bring to a boil. Break up the insoluble portion with a stirring rod and again bring to a boil; titrate back with tenth-normal alkali. Subtract the amount of alkali required from the 10 cc. of acid used and multiply the remainder by 2 to find the alkalinity of the water-insoluble portion. Use phenolphthalein as indicator. To the portion soluble in water add 10 cc. of tenth-normal sulphuric acid and bring to a boil. Titrate back with tenth-normal alkali using phenolphthalein as indicator. Subtract the number of cubic centimeters required to titrate back from 10 and multiply by 2 to find the alkalinity of the water-soluble portion. The total alkalinity of the ash is the sum of the alkalinity of the water-insoluble portion and the alkalinity of the water-soluble portion.

The following terms may be used in the calculations:

(a) The acidity of the tartaric acid contained in 100 cc. of wine expressed in terms of tenth-normal acid.

(b) The total alkalinity of the ash expressed in terms of tenth-normal acid.

(c) The alkalinity of the water-soluble ash expressed in terms of tenth-normal acid.

(d) The alkalinity of the water-insoluble ash expressed in terms of tenth-normal acid.

To find (a), divide the total tartaric acid content in 100 cc. of wine by 0.015. With the help of these terms (a), (b), (c), (d), the tartaric acid in the free state, and as cream of tartar, may be figured in the following manner:

(1) If (a) is greater than (b):

Cream of tartar = 0.0188 × (c),

Free tartaric acid = 0.015 × [(a) − (b)],

Tartaric acid to alkaline earths = 0.015 × (d).

(2) If (a) equals (b) or smaller than (b); but greater than (c):

Cream of tartar = 0.0188 × (c),

Free tartaric acid = 0,

Tartaric acid to alkaline earths = 0.015 × [(a) − (c)].

(3) If (a) is smaller than (c):

Cream of tartar = 0.0188 × (a),

Free tartaric acid = 0,

Tartaric acid to alkaline earths = 0.

Example:

Total tartaric acid = 0.680 grams per 100 cc.

Total alkalinity = 31.0 cc. of tenth-normal acid.
Water-soluble alkalinity = 24.6 cc. of tenth-normal acid.
Water-insoluble alkalinity = 6.4 cc. of tenth-normal acid.

(a) $= \frac{0.680}{0.015} =$ 45.3 cc. of tenth-normal acid.
(b) = 31.0 cc. of tenth-normal acid.
(c) = 24.6 cc. of tenth-normal acid.
(d) = 6.4 cc. of tenth-normal acid.

In this case (a) is greater than (b), therefore, 24.6 × 0.0188 = 0.46 grams per 100 cc. of cream of tartar; (45.3 − 31.0) × 0.015 = 0.21 gram per 100 cc. of free tartaric acid; 6.4 × 0.015 = 0.10 gram per 100 cc. of tartaric acid to alkaline earths.

To be assured that the tartaric acid added in the Hartmann and Eoff modified method is pure, it is advisable to titrate 0.1500 gram of the dried acid with tenth-normal sodium hydroxid using phenolphthalein as an inside indicator. This should require 20 cc. of the soda. In reporting your results please enclose this titer on the 0.1500 gram of tartaric acid.

RESULTS OF COÖPERATIVE WORK.

The following tables give the results obtained by four of the collaborators:

Coöperative work on tartaric acid.

SAMPLE NO. AND ANALYST	TOTAL TARTARIC ACID		CREAM OF TARTAR	FREE TARTARIC ACID	
	Bulletin method	Hartmann and Eoff method		Bulletin method	Hartmann and Eoff method
	gram per 100 cc.	*gram per 100 cc.*	*gram per 100 cc.*	*gram per 100 cc.*	*gram per 100 cc.*
SAMPLE 1:					
H. L. Lourie, New York, N. Y.	0.17	0.18	....	....	....
J. R. Eoff, Jr., Washington, D. C.	0.17	0.17	0.05	0.05	0.05
M. J. Ingle, Washington, D. C.	0.18	0.19	0.05	0.07	0.08
H. C. Fuller, Washington, D. C.	0.19	0.20	0.04	0.08	0.09
Average	0.18	0.19	0.05	0.07	0.07
SAMPLE 2:					
H. L. Lourie, New York, N. Y.	0.43	0.45	....	....	....
J. R. Eoff, Jr., Washington, D. C.	0.41	0.45	0.06	0.29	0.34
M. J. Ingle, Washington, D. C.	0.45	0.48	0.06	0.33	0.37
H. C. Fuller, Washington, D. C.	0.45	0.49	0.04	0.33	0.37
Average	0.44	0.47	0.05	0.32	0.36

Results on alkalinity of ash.
(cc. tenth-normal acid per 100 cc. wine).

ANALYST	SAMPLE 1		SAMPLE 2	
	Soluble alkalinity	Insoluble alkalinity	Soluble alkalinity	Insoluble alkalinity
J. R. Eoff, Jr., Washington, D. C.	2.7	5.0	3.0	4.4
M. J. Ingle, Washington, D. C.	2.8	5.0	3.0	4.8
H. C. Fuller, Washington, D. C.	2.2	5.0	2.3	5.7
Average	2.6	5.0	2.8	5.0

It is evident from the figures in the tables submitted that the determination of tartaric acid as described in Bulletin 107, Revised, gives results materially too low and that the proposed method gives results which are very close to the truth.

The average content of total tartaric acid in the straight wine No. 1, determined by both bulletin and proposed methods is 180 and 190 mg., or 185 for the average of both methods. Accordingly, wine No. 2, which is wine No. 1 to which 300 mg. of tartaric acid were added, should show 485 mg.

The following are the results obtained by the methods under discussion:

Results on total tartaric acid.

ANALYST	TOTAL TARTARIC ACID	
	Bulletin method	Hartmann and Eoff method
	mg. per 100 cc.	*mg. per 100 cc.*
H. L. Lourie, New York, N. Y.	430	450
J. R. Eoff, Jr., Washington, D. C.	410	450
M. J. Ingle, Washington, D. C.	450	480
H. C. Fuller, Washington, D. C.	450	490
Average	435	468

From these determinations, it will be seen that, although the results of the several analysts are not concordant, the bulletin method consistently gives results which are lower than those obtained by the proposed method and that the bulletin method out of a total of 485 yields only 435, and proposed method 468 mg. of tartaric acid.

NOTES BY THE COLLABORATORS.

M. J. Ingle: In all ash work it was found essential to burn off in an electric muffle at a "dead heat" or one that could not be distinguished by sight, in order to prevent fusing. In the tartaric acid determination by the method outlined in Bulletin 107, Revised, the time of stirring was lengthened to about 2 minutes, as in cases where small amounts of tartaric acid were present it was found necessary to positively start the formation of the precipitate. In drying the tartaric acid used in the modified method, a Petri dish was found to be a convenient and useful container as the powdered dried acid will keep dry for days in it.

It was suggested to try out the addition of a neutral tartrate instead of using the free acid as used in the proposed method outlined by Hartmann and Eoff, the original intent being to have the neutral tartrate take care of all free tartaric acid. In order that a salt available to most chemists might be used, Rochelle salt was chosen. As this salt contains 4 mole-

cules of water of crystallization, drying in an oven was found to be impracticable. Drying in a desiccator was next tried, but even in this mild dehydrating atmosphere, the salt was found to lose 12 per cent of its weight in a short period of 30 hours. It was decided to use the pure salt as received and run a blank with each series of determinations. Two blank determinations on the same weight of salt were tried by the bulletin method with the omission of potassium acetate; to one enough free tartaric acid was added to just form the acid salt; in the second the same object was accomplished, depending upon the 2 cc. of acetic acid to form the acid salt. Both procedures yielded excellent results, giving nearly perfect yields of tartaric acid. The fact that only 53.17 per cent of the weight used is tartaric acid, makes accurate additions of tartaric acid easier by this means. A wine containing 0.20 gram per 100 cc. of free tartaric acid in addition to about 0.22 of combined acid was used for the experiment. The wine was titrated for total acidity and the factor for determining the addition of Rochelle salt was calculated to be 0.1409 times the number of cubic centimeters of normal alkali found to be necessary for complete neutrality.

It developed in the course of these determinations that the recovery of tartaric acid was not complete in the determinations on wine when the acidity was not first neutralized, so that the experiment did not prove successful in doing away with the neutralizing, but was shown to be of material benefit as suggesting Rochelle salt as a stable and efficient means of introducing weighed amounts of tartaric acid into the completely neutralized wine or grape juice.

In the following determinations the bulletin method was used, omitting the addition of potassium acetate in all but B. In A and B the wine was completely neutralized, C was not neutralized. Determinations I and II are the blanks to which reference has been made.

Determination of tartaric acid using Rochelle salt.

SUBSTANCE	DETERMINATION	ROCHELLE SALT ADDED	TOTAL TARTARIC PRESENT	TARTARIC ACID RECOVERED	ORIGINAL TARTARIC ACID CONTENT
		gram per 100 cc.	*gram per 100 cc.*	*gram per 100 cc.*	*gram per 100 cc.*
Wine	A	0.793	0.842	0.838	0.416
Wine	B	0.793	0.842	0.836	0.414
Wine	C	0.793	0.842	0.800	0.378
Solution	I	0.793	0.845	0.841	0.422
Solution	II	0.793	0.422	0.428	.....

The relative efficiency of the Hartmann and Eoff modification and Kling's rocemate method (*Annales des Falsifications*, 1910, p. 239; 1911, p. 185) was tried out in the Charlottesville laboratory. Two wines rep-

resenting the extremes in the ratio of free to combined tartaric acid were used. Sample 2096 contained 0.31 gram per 100 cc. of free tartaric acid out of a total of 0.53; the second sample (3262) had a total of 0.34 of which only 0.05 was free. The principle of the Kling method is the formation of calcium rocemate in a favorable medium for a very complete precipitation. This is accomplished by adding lime and laevo tartrate of ammonia in suitable quantities and titrating the calcium rocemate with permanganate. The time factor is in favor of this method, but owing to the expense of the left tartrate and the fact that the tartrate solutions are not stable, the Hartmann and Eoff method appears to be the more practicable for most laboratories, especially those not possessing a microscope.

The following table is self-explanatory; 25 cc. of wine were used in each determination:

Comparison of the Kling and the Hartmann and Eoff methods for total tartaric acid.

SAMPLE NO.	TESTS	TOTAL TARTARIC ACID	
		Kling method	Hartmann and Eoff method
		gram per 100 cc.	*gram per 100 cc.*
2096	1	0.559	0.53
	2	0.554	
	3	0.547	
	4	0.554	
	Average...........	0.553	
3262	1	0.342	0.34
	2	0.344	
	3	0.347	
	4	0.337	
	Average...........	0.342	

J. R. Eoff, jr.: It was found that a very simple modification of the usual method for tartaric acid determination or of the recently proposed method of Hartmann and Eoff will enable an analyst in most cases to determine the total tartaric acid content of a wine or grape juice in less than one hour's time. The major portion of the time ordinarily necessary for a tartaric acid determination is the 15 or more hours that the solution is allowed to stand to accomplish complete precipitation. This period may be reduced to 15 to 30 minutes, depending upon the amount of tartaric acid present, by the use of a mechanical stirrer. The following table will illustrate the practicability of substituting the stirrer for the longer method of precipitation:

Determination of tartaric acid using a mechanical stirrer.

SUBSTANCE	TARTARIC ACID CONTENT	HARTMANN AND EOFF METHOD	HARTMANN AND EOFF METHOD; STIRRED 30 MINUTES	HARTMANN AND EOFF METHOD; STIRRED 15 MINUTES
	gram per 100 cc.	*gram per 100 cc.*	*gram per 100 cc.*	*gram per 100 cc.*
Tartaric acid solution	0.481	.....	0.482	.....
do	0.481	.....	0.483	.....
do	0.241	.....	.....	0.238
do	0.241	.....	.....	0.236
do	0.241	.....	.....	0.238
do	0.120	.....	.....	0.110
do	0.048	0.042	0.025	.....
do	0.048	0.042	[1]0.012	.....
California Hock wine	[2]0.254	0.240	0.246 0.264	.....
California Sauterne	[2]0.221	0.215	0.218 0.216	.....
California Zinfandel	[2]0.233	0.211	0.240 0.246	.....
California Sherry	.....	0.088	0.100 0.099	.....
California Port	.....	0.113	0.122	.....
California Sherry No. 2	.....	0.101	0.101 0.099	.....
California Port No. 2	.....	0.120	0.120	.....

[1] Stirred 60 minutes. [2] Content determined by bulletin method.

As can be seen it is possible to determine accurately as little as 0.1 gram per 100 cc. of tartaric acid in less than an hour by the use of the Hartmann and Eoff modification of the bulletin method if the mechanical stirrer is used in conjunction therewith. For amounts of tartaric acid materially less than 0.1 gram per 100 cc., it is not advisable to make use of the shortening of the time, since even with an hour's stirring the precipitation is incomplete. The stirring apparatus is so well known that a description would be superfluous. The speed of stirring used in the above tests was as high as could be applied without loss of solution by spattering. It is suggested that, in the absence of a stirring apparatus, a bottle containing bits of glass rod or glass beads would answer the same purpose if the solution under examination were placed therein and vigorously shaken during a similar period. The application of the stirrer points out additional advantage of the Hartmann and Eoff method, that of furnishing quickly the tartaric acid content of low acid wines.

NOTES BY THE REFEREE.

The reports by the four collaborators show that the modified method by Hartmann and Eoff gives very satisfactory results and that the bulletin method is not reliable in cases where much free tartaric acid is present in a wine. Before proposing the method for adoption as a provisional method, more work should be done especially as to its applicability to red wines.

The report of M. J. Ingle furnishes additional evidence that the proposed method gives highly satisfactory results. In his report he shows that determinations of tartaric acid made in two wines by the proposed method and the Kling rocemate method give very close checks.

A very interesting contribution to the method of tartaric acid determination is made in this report, wherein a neutral salt of tartaric acid is substituted in place of the tartaric acid addition, as provided in the Hartmann and Eoff method. This modification of the proposed method should be more thoroughly investigated, because it may prove to be a more desirable procedure than the proposed one.

As regards the report by J. R. Eoff, jr., it should be said that the method is a valuable contribution because it makes quick work a possibility without forfeiting accuracy, in all cases where amounts of tartaric acid greater than 0.10 gram per 100 cc. are present in the liquid under examination.

REPORT ON BEER.

By J. G. Riley, *Associate Referee.*[1]

The work on beer consisted in making a critical study of the provisional method for phosphoric acid (Bur. Chem. Bul. 107, Rev., p. 92), and a comparison of this method with other methods as to accuracy and time of determinations.

Two samples of beer, a malt beer marked No. 1, and a beer made from 55 per cent of malt (by weight) and 45 per cent of corn, marked No. 2, were submitted to collaborators to determine phosphoric acid expressed as milligrams of phosphoric acid per 100 cc. by the following methods:

METHODS FOR COÖPERATIVE STUDY.

Method 1.—Uranium acetate method: Bureau of Chemistry Bulletin 107, Revised, page 92, article 15.

Method 2.—Measure 25 cc. of the beer, 15.6°C., free from carbon dioxid, evaporate and ash at a low red heat. Transfer with dilute nitric acid to an Erlenmeyer flask and proceed according to Bulletin 107, Revised, page 4, No. 2 (b_1), Total Phosphoric Acid.

Method 3.—Measure 25 cc. of the beer, 15.6°C., free from carbon dioxid gas, and add 25 cc. of standard calcium acetate. Prepare calcium acetate as given in Bulletin 107, Revised, page 21, 2 (a). Evaporate and ash and proceed as in Method 2.

Method 4.—Wet combustion method: Measure 25 cc. of the beer, 15.6°C., free from carbon dioxid, into a 500 cc. Erlenmeyer flask, and proceed according to Bulle-

[1] Read by M. J. Ingle.

tin 107, Revised, page 2, Total Phosphoric Acid (a_5), and then according to page 5, 2 (b_1), Total Phosphoric Acid.

The collaborators were requested to note also the effect of corn upon the amount of phosphoric acid in the beer. Reports of seven collaborators are tabulated as follows:

RESULTS OF COÖPERATIVE WORK.

Coöperative results on phosphoric acid in beer. (mg. per 100 cc.)

COLLABORATOR	PHOSPHORIC ACID							
	Method 1		Method 2		Method 3		Method 4	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
R. W. Hilts, Seattle, Wash.	90.6	53.3	90.7	46.0	[1]101.6	[1]46.9	[2]90.9	....
	90.6	53.3	91.1	45.9	[1]101.2	[1]47.2	[2]88.5	....
	...	....	...	....	101.4	47.4	[3]95.3	[3]43.9
	...	....	...	....	101.0	46.9	[3]84.0	[3]44.0
	...	....	...	....	.....	....	[4]101.2	[4]44.9
	...	....	...	....	.....	....	[4]101.3	[4]45.6
H. C. Fuller, Washington, D. C.	....	50.0	91.2	54.4	101.2	48.8	94.4	44.0
S. H. Ross, Omaha, Nebr.	90.7	46.5	100.9	47.8	100.3	48.3	.....	....
H. B. Mead, Philadelphia, Pa.	108.1	48.8	58.1	50.2	103.8	51.4	48.2	44.0
	100.7	47.7	54.1	47.4	103.0	52.8	77.8	45.6
	90.1	....	62.7	....	104.3	....	90.4	....
	91.2	....	59.6	....	102.4	....	80.2	....
E. Pettijohn, St. Paul, Minn.	101.0	49.0	53.0	47.0	104.0	47.0	101.0	45.0
E. Grab, Nashville, Tenn.	88.1	48.5	87.9	45.3	90.6	45.5	91.0	45.5
	88.2	48.6	....	....	....	....	.....	....
J. G. Riley, Washington, D. C.	102.4	51.4	42.6	44.0	99.6	46.0	102.4	48.4

[1] Unburned carbon particles not burned out.
[2] Using nitric acid and hydrochloric acid only.
[3] Using nitric acid, hydrochloric acid and sulphuric acid.
[4] Using nitric acid and sulphuric acid only.

COMMENTS OF ANALYSTS.

R. W Hilts: In Method 1 the uranium solution described by Sutton ("Vol. Anal.," 10th ed., p. 309) was used and standardized on a solution of microcosmic salt under the same conditions as in titrating the beer. The microcosmic salt solution was standardized gravimetrically by the magnesia method. The good agreement of duplicates is accidental as the end point could hardly be determined closer than 0.25 cc., which means an experimental error of ± 5 mg. of phosphoric acid per 100 cc. of beer. This method gives erroneous results and is wholly unsuited to the estimation of such small amounts of phosphoric acid.

Method 2 is better, but there appears to be a loss of phosphorus in the all malt beer.

Method 3 gives excellent results. In the determinations marked [1] the unburned carbon particles were not filtered out, which made the end point a little difficult in

the titration. In the other cases the nitric acid solutions of the ash were filtered through paper, the paper washed and ashed and the residue taken up in acid and added to the main solution.

In Method 4 in determinations marked [2], this laboratory used 30 cc. of nitric acid and 5 cc. of hydrochloric acid, boiling down to a small volume and then diluting and proceeding to the precipitation, just as directed (a_5). This does not destroy all organic matter and the result appears to be low. In determinations marked [3] the same amounts of acid were used but 8 cc. of sulphuric acid were added and organic matter was totally destroyed by one or two further additions of nitric acid, after evaporation to sulphur trioxid fumes. In determinations marked [4] the beer was put in a 500 cc. Kjeldahl flask with 30 cc. of nitric acid and 8 cc. of sulphuric acid and was gently boiled down to the trioxid fumes, when all organic matter was destroyed without further additions of acid or any attention. I think this is the most convenient method of performing the wet combustion. In [3] and [4], finally 25 to 30 cc. of water were added, the solution boiled for several minutes, and then rinsed into beakers, which were used in all cases instead of flasks, for the molybdate precipitations. The phosphomolybdate precipitates were filtered on asbestos and, for washing, water containing a little ammonium nitrate was used. There is then no danger of the precipitate washing through the filter in a colloidal condition, as often happens with plain water.

In my opinion, Method 4[4], destroying all organic matter, is preferable to Methods 1 and 2 in point of accuracy, and to Method 3 in ease of manipulation.

H. C. Fuller: It is evident that the presence of corn materially reduces the content of phosphoric acid. Method 1 is of no value with dark beers and ought not to be recommended as a method which might at any time be made the basis of a court procedure. One is not sure of his end point within 5 cc. in either direction. The prevailing opinion in this laboratory is in favor of Method 3.

S. H. Ross: In Method 1, the titration factor is too large to allow close determination of the phosphoric acid. In Method 2, by ashing at a low temperature in an electric muffle, the use of calcium acetate prescribed in Method 3 appears unnecessary. In Method 4, the formation of the yellow precipitate was very slow; after standing 45 minutes and filtering, further precipitation occurred in the filtrate. There appears to be no advantage in the wet combustion method over the direct incineration and the method was abandoned without ascertaining the cause of incomplete precipitation.

H. B. Mead: Of the four methods, Method 3 appears the most accurate in consistently giving the highest results obtained. The possible reason for this is that the calcium acetate might assist in retaining the organic phosphorus. The provisional uranium acetate method apparently indicates about 90 per cent of the total phosphoric, assuming that Method 3 yields the correct figure. For Method 4 would say that results on Sample 2 should probably be thrown out, as the Erlenmeyer flasks containing 25 cc. of sample, 30 cc. of concentrated nitric acid, and 5 cc. of concentrated hydrochloric acid were heated on the steam bath for some hours before digestion over a flame. All portions of Sample 1 for treatment by Method 4 were measured out before Sample 2 was opened, which eliminates the possibility of confusion in marking. No explanation is offered for the low results obtained on Sample 1, Method 4. The analysis proceeded smoothly at all stages. Digestion was made with a low flame.

Method 1 is, of course, the quickest, requiring about 15 minutes after the beer has been freed of the gas and providing the volumetric solution is ready for use. Methods 2 and 3 take a little over one working day as it was hardly possible to do

more than evaporate and ash in less than 7 hours. Ashing in Method 2 was more rapid than in 3 as the calcium salts seemed to prevent speedy oxidation by the latter method. In fact, an entirely white ash was obtained in none of the determinations tried by this method, although the ash was moistened repeatedly. Moistening the ash with nitric acid might shorten the time and should give a white ash. Method 4 consumed about 2 hours, the oxidation being complete in about 1 hour. More vigorous boiling might shorten the time, but no information is available concerning the effect of such treatment on the results.

The lack of agreement in Method 4 on Sample 1 may be due to inexperience with the method.

E. Pettijohn: In conducting the determination according to Method 1, some difficulty was experienced in judging the correct end point of the titration. This was especially the case with Sample 1. It seems desirable in working on beer to make a trial titration according to the procedure described in the official method, then repeat the titration, adding 2 to 3 drops of the standard uranium acetate solution at a time toward the last. The characteristic end-point indication will finally develop and no serious difficulty should be noted.

In working with Sample 1 according to Method 2, low results were obtained. The sample was reduced to ash in two different ways, first over an open flame under a cover of platinum foil, then in an electric muffle. The same results were obtained by each procedure. No reason can readily be assigned for the low results on Sample 1 by this method. They are nearly as low as results obtained by the same method on Sample 2.

In applying Method 4 to Sample 1, it was found necessary to repeat the treatment and evaporation with the acid mixture, as the single treatment appeared to be quite inadequate to get the sample in right condition. The results turned out satisfactorily, duplicate determinations agreeing very closely.

Of the four methods subjected to trial, Method 1 is preferred, chiefly because it was found possible under ordinary conditions to complete the two determinations inside of a half hour. The time required by any one of the other three methods varied from four to five hours. Method 4 would be second in order of preference. Each of the results reported in the above tabulation is an average of two or three closely-agreeing check determinations. The peculiarity noted in the results obtained by Method 2 on Sample 1 is a matter that does not seem to be easily explained. The results, however, are as correct as could be obtained, in this as well as in the other determinations reported in the table.

E. Grab: In Method 1, I wish to call attention to the fact that the uranium acetate solution is standardized against a colorless phosphate solution. The method used in this standardization is that given in Sutton's "Volumetric Analysis," 10th edition, Phosphoric Acid and Phosphates, page 308, paragraph 2, and page 309, paragraph 3. There is a decided color present in the beer, and in titrating this against the uranium acetate, it will be on a different basis than the standardization of the uranium acetate. The amount of uranium acetate used is small in comparison to the amount of beer taken. No investigation has been made to determine whether using a more dilute solution will affect the method. If not, I should judge that a solution about half as strong as given in Sutton would be more accurate. Because of the color present in the beer, determination of the end point requires practice. The two results given by me on both of these beers in this method are fairly close. Considering that the standard solutions are already made, the method is a very quick one, taking less time than the other three methods.

Method 2 is similar to the method used in this laboratory for the determination of phosphoric acid in vinegar. I consider it accurate if the heat is kept down when

the ash is burned. I wish to call attention to the precipitation of the ammonium phosphomolybdate. If certain conditions are not followed, this precipitate is too fine and passes through the filter.

Method 3 is practically identical with Method 2, the only difference so far as I can see being the longer time it takes to evaporate. I fail to see anything gained by the addition of the calcium acetate unless it is the fact that the beer is ashed in less time, and that the chances of losing phosphoric acid by too high heat is less.

Method 4 is no more accurate, in my opinion, than either 2 or 3. The process of destroying organic matter by the addition of nitric acid, hydrochloric acid, and heat, brings in several factors which I consider objectionable—the large amount of fumes and the risk of the vessels breaking. I found also that if all organic matter was not destroyed, the results obtained are low, and that it took several additions of nitric acid and hydrochloric acid to destroy all this organic matter. I am of the opinion that if this method is followed, it is best to evaporate the beer in the flask nearly to dryness, then to digest. The time taken, following Method 4, is decidedly longer than that by any of the other methods.

Referring to the enclosed sheet which contains the values obtained by these different methods, I wish to call attention to the fact that I found that the addition of corn meal lowered the total phosphoric acid 48.3 per cent. In both samples the results obtained with Methods 3 and 4 compare favorably. In Sample 1, the results with Methods 1 and 2 are fairly close. In Sample 2, the results obtained with Method 1 are higher than those obtained with any of the other methods. All measurements were made at 20°C.

DISCUSSION OF RESULTS.

An inspection of the table indicates that Method 3 gives the most concordant results. Although this determination takes from 4 to 5 hours, the actual time of manipulation is not more than 20 minutes. It was checked with the gravimetric method as follows: Duplicates of Samples 1 and 2 were analyzed by F. W. Smithers and E. L. Wilcox, Bureau of Chemistry, according to Method 3. The ash was taken up with water and nitric acid, filtered, and washed; residue burned, and again taken up with dilute nitric acid and added to the main portion. The phosphoric acid was then precipitated as ammonium phosphomolybdate, and finally weighed as magnesium pyrophosphate as follows: Weight of magnesium pyrophosphate 0.0383 and 0.0392 gram in Sample 1, 0.0172 and 0.0190 gram in Sample 2; corresponding to the weight of phosphoric acid in 25 cc., 0.02443 and 0.02500, [1]0.01097 and 0.01211; which equals milligrams of phosphoric acid in 100 cc., 97.72 and 100.00, ——, and 48.44.

These gravimeteric determinations were repeated, using Method 4 for the oxidation of the organic matter, with the following results: Weight of magnesium pyrophosphate 0.0386 and 0.0388 gram in Sample 1, 0.0180 and 0.0178 gram in Sample 2, corresponding to the weight of phosphoric acid 0.02462 and 0.02474, 0.01148 and 0.01135; which equals milligrams of phosphoric acid per 100 cc., 98.48 and 98.96, 45.92 and 45.40.

[1] Discarded, loss of precipitate.

From observation of the gravimetric determinations, it is seen that the concordant results of Method 3 agree with the gravimetric results, within experimental error.

During the last three years, Method 4 has been used in the Bureau of Chemistry and found to check with the gravimetric method. From the tabulated results, however, it is readily seen that it is a method which requires more experience to obtain correct results than Method 3. Therefore, Method 3 is preferable.

Method 2 is an uncertain method, with a great danger of loss of phosphoric acid and should be abandoned.

Method 1 appears to be accurate for light beers, but dark beers have to be diluted many times in order to get a proper end point and results are uncertain.

Therefore, it is recommended that Method 3 be adopted, in place of Method 1, as the official method in the determination of phosphoric acid in beers.

The effect of corn in lowering the amount of phosphoric acid present in the beer is also to be noted.

Your attention is called to corrections which should be made in the dextrin determination as given on page 91 of Bulletin 107, Revised. The phrase "in the original beer," in line 6, evidently means in the beer after hydrolyzing, and the final word of the method should be "beer" and not wort.

"Multiply the amount of maltose in the original beer by the factor [1]1.053 and substract this from the total amount of dextrose found after hydrolyzing, and multiply the remainder by 0.9, giving the dextrin in the original beer."

The factor 1.053 takes account of the fact that 19 parts of maltose yield 20 parts of dextrose after hydrolyzing with dilute acid. The factor given in Bulletin 107, Revised, is the reciprocal of the proper factor. For an example of this calculation correctly stated see Koenig, *Untersuchung Landwirtschaftlich und Gewerblich Wichtiger Stoffe*, 3d Ed., page 665.

REPORT ON DISTILLED SPIRITS.

By A. B. Adams, *Associate Referee.*

As no work had been planned for the past two years the present associate referee had no unfinished work to take up.

Chemists who have done much spirit analyses know that excessive amounts of aldehydes in the spirit, if not removed, are extracted, oxidized,

[1] This is on the assumption that the anhydrous maltose table is used. This factor, however, can not be less than 1.000 nor more than 1.053.

and titrated, raising the final result higher than is correct for the method used. It was thought that this error would be a good one to take under consideration for 1913.

J. M. Doran, of the Bureau of Internal Revenue and the associate referee, did a certain amount of preliminary work, in order to find a basis for collaboration. In this way the amount of work required was reduced to a minimum.

Briefly, this preliminary work consisted in adding to two samples of distilled spirits containing aldehydes, varying amounts of m-phenylenediamin hydrochlorid, determining the amount of aldehydes left therein, and the effect of these aldehydes on the fusel oil results. It showed that, saponification with sodium hydroxid removed a portion of the aldehydes; when aldehyde content was about 20 parts per 100,000 it removed about three-quarters; and that increasing amounts of this m-phenylenediamin hydrochlorid had to be added as the content of aldehyde increased; 0.2 of a gram seemed to be satisfactory for contents of about 20 parts of aldehyde and 0.5 was found to be sufficient for excessive amounts.

Two samples were prepared and sent to those collaborators who had signified their willingness to assist, with the request that the fusel oil determination be made in these samples as given in Bulletin 107, Revised, page 98, then the sample be treated by the following method:

After the esters are saponified and the spirit distilled, add 0.5 gram of m-phenylenediamin hydrochlorid, reflux for one hour, redistill, and proceed as usual.

Sample 1 was a so-called brandy called "Grappa," which is used a great deal in California and which always contains large amounts of aldehydes. The aldehyde content of this sample was 151 parts per 100,000.

Sample 2 was made from alcohol, amyl alcohol, and aldehydes. The aldehyde content was 28.7 parts per 100,000.

Coöperative results on determination of fusel oil.

ANALYST	FUSEL OIL BY ALLEN-MARQUARDT METHOD			
	Sample 1		Sample 2	
	Untreated	Treated	Untreated	Treated
W. W. Karnan, Cincinnati, Ohio	269.0	109.0	97.0	68.0
J. I. Palmore, Washington, D. C.	278.6	102.7	108.5	76.5
J. M. Doran, Washington, D. C.	348.0	98.3	76.6	61.5

It is not necessary to dwell on these results; they show clearly that when 20 parts of aldehyde are present the result is appreciably affected,

and that when larger amounts are present the result obtained by the untreated method is hopelessly incorrect.

The associate referee has the honor to submit the following recommendation, that the Allen-Marquardt method for fusel oil determination be modified as given in Bulletin 107, Revised, page 98 (b) Allen-Marquardt method, fourth line after "is collected" by adding "Whenever aldehydes are present in excess of 15 parts per 100,000, to distillate add 0.5 gram of m-phenylenediamin hydrochlorid, reflux for one hour, distill 100 cc., add 25 cc. of water and continue distillation until an additional 25 cc. is collected."

It is recommended further that the associate referee be directed to confer with the chemists, engage in spirit analysis, do such collaborative work as necessary, and submit at the next meeting a revised Allen-Marquardt method containing such change in details and manipulation as experience justifies.

REPORT ON VINEGAR.[1]

By E. H. Goodnow, *Associate Referee.*

No collaborative work on vinegar has been undertaken this year. The referee work of the association for the past two years has been given over to a general and very complete revision of the methods of analysis, which has resulted in a modification of the official and provisional methods as published in Bulletin 107, Revised, in the application of a number of standard determinations to the analysis of vinegar, and in the development of new tests which have been found of value in detecting adulteration or establishing the purity of a sample. This completed scheme of examination is given in the Proceedings of the association for 1911 (Bur. Chem. Bul. 152, pp. 126–7).

These methods of analysis have been submitted to collaborative examination in connection with the referee work. Their reliability has been further established in the very large number of check analyses made in connection with the official inspection work of the Bureau of Chemistry. The recommendations of the referee that several of these methods be further studied were not carried out, owing to the fact that the present referee was appointed as a substitute for the original referee too late to give opportunity for the necessary preliminary work for the development of a scheme of investigation, which would be of value in studying these methods. It is, therefore, recommended that a study of the methods suggested by the referee for 1912 be included in the collaborative work of the association for the following year.

[1] Not read at this meeting.

REPORT ON FLAVORING EXTRACTS.

By A. E. Paul, *Associate Referee.*[1]

The collaborative work this year was confined to two extracts, vanilla and peppermint. In planning the work, the suggestions of last year's referee were adhered to quite closely.

VANILLA EXTRACT.

COMPOSITION OF AUTHENTIC VANILLA EXTRACTS.

In following the recommendation for a further study of the composition of pure commercial vanilla extracts, it seemed desirable to secure analyses of extracts prepared from the greatest variety of beans, prepared by as many different methods as possible. To do this, each collaborator was requested to either make or obtain elsewhere extracts of absolutely known origin, and report his results, obtained by the official methods. Unfortunately very few responses were received to this request. The results and comments of the collaborators follow:

Collaborator's analyses of authentic samples of vanilla extracts.

DETERMINATION	A. W. HANSON		H. J. WICHMANN	B. B. WRIGHT		H. E. WOODWARD			
	Mexican (U. S. P.)	Tahiti and Bourbon (U. S. P.)	Bourbon	Mexican (U. S. P.)	Bourbon (U. S. P.)	Mexican (U. S. P.)		Extracts prepared from the exhausted beans	
						A	B	A	B
Specific gravity at 15.6 C	....	....	......	......	......	1.009	1.0104	....	....
Vanillin (gram per 100 cc.)	0.20	0.14	0.25	0.2128	0.2992	0.28	0.23	0.049	0.051
Lead number	0.51	0.50	0.65	0.4727	0.6448	0.74	0.76	0.10	0.10
Color extract, red	....	....	50.	......	......	[1]175.	[1]185.	[1]112.	[1]110.
Color extract, yellow	....	....	122.	......	......	....	....	....	....
Color filtrate, red	....	....	1.7	......	......	12.	16.	4.	4.
Color filtrate, yellow	....	....	7.0	......	......	....	....	....	....
Color in filtrate, red	....	....	3.4	......	......	6.9	8.7	3.6	3.6
Color in filtrate, yellow	....	....	5 8	......	......	....	....	....	....
Color insoluble in amyl alcohol (per cent)	....	....	19.0	......	......	18.	20.	5.2	5.5
Alcohol (per cent by volume)	...	..	43 6	...	...	53.	53.	....	....
Ash (grams per 100 cc.)	....	....	......	......	......	0.40	0.40	0.10	0.10
Solids (grams per 100 cc.)	....	....	3.9	......	......	23.2	23.6	1.08	0.29
Sugars (grams per 100 cc.)	....	....	0.7	......	......	21.3	21.8	0.83	0.08

[1] Brewer's scale.

The extracts examined by *A. W. Hanson* were manufactured by Ridenour Baker Grocery Company, Kansas City, Mo. The Mexican extract was prepared from 40

[1] Read by Julius Hortvet.

pounds of prime Mexican beans to 50 gallons of finished product with 25 pounds of sugar. The Tahiti and Bourbon was made from 35 pounds of Tahiti, 6 pounds of Bourbon, and 25 pounds of sugar. The ingredients were macerated three months or over in 25 gallons of alcohol and 15 gallons of water, drawn off, diluted to 50 gallons, and allowed to settle.

H. J. Wichmann's samples were manufactured by Brown Brothers Mercantile Company, Denver, Colo., from 12 ounces of Bourbon cuts per gallon of alcohol diluted half with water. These were digested at 110°F. for 24 hours in a machine made by the Hardesty Company. After completion of the process a little sugar was added.

B. B. Wright reports that the Mexican beans were imported from Vera Cruz, Mexico. They were high grade and of uniform length, averaging 20 cm. In making the extract the only deviation from the U. S. P. was that 3 days instead of 24 hours were consumed for percolating the extract. The Bourbon beans were declared by the shipper to have been grown in Reunion and Madagascar. In making the extract, the percolation was continued for 3 weeks, thus extracting quite completely all valuable ingredients.

The extracts examined by *H. E. Woodward* were made in the laboratory by C. S. Brinton from high grade Mexican beans, which had become much dried out and brittle in the laboratory. The original extracts were made according to the U. S. P. The dregs were macerated and percolated with 60 per cent alcohol to one-half the volume of the original extract. The results on these second extracts should, therefore, be divided by two in order to place them on the same basis as the original extracts, or for comparison with the results obtained by Winton and Berry (Bur. Chem. Bul. 162).

WICHMANN'S QUALITATIVE COUMARIN METHOD.

Wichmann's qualitative coumarin method originally appeared in Bureau of Chemistry Circular 95. Since its publication the author has slightly modified the directions to read as follows:

Slightly acidify 25 cc. of the extract, if alkaline, with sulphuric acid, add 25 cc. of water, and distill until yellow decomposition products appear. To the distillate, containing the vanillin and coumarin, add 15 to 20 drops of 1 to 1 potassium hydroxid, hastily evaporate the distillate to 5 cc., and transfer to a test tube. Heat the test tube over a free flame until the water completely evaporates and the residue fuses to a colorless, or nearly colorless, mass. Coumarin, if present, will be converted into potassium salicylate. If decomposition products have been allowed to distill over, the potassium hydroxid solution will become yellow, turning black as the fusion point is reached. In this case the fusion will not become colorless, but usually an appreciable diminution of the black color will be observed. It is well to add more potassium hydroxid when decomposition products are present to prevent the danger of burning the salts to a char. Cool the melt and dissolve in a few cubic centimeters of water. Transfer the solution to a 50 cc. Erlenmeyer flask and acidify slightly with 25 per cent sulphuric acid. The amount of solution should not be over 10 cc. Finally distill the solution into a test tube containing four or five drops of neutral 0.5 per cent ferric sulphate or ferric chlorid. The efficiency of the reagent should be tested by a few cubic centimeters of a solution containing not more than 0.1 mg. of salicylic acid per cubic centimeter. If coumarin is present in the original

extract, an amethyst or purplish color will develop, the intensity being directly proportional to the amount of coumarin.

This method and two samples were submitted to the collaborators. The samples consisted of a true U. S. P. vanilla extract, with and without the addition of 0.01 per cent of coumarin.

The collaborators were requested to apply Wichmann's method, reporting results as "positive" or "negative," and to make a statement as to whether, in the routine examination of miscellaneous vanilla extracts, genuine and artificial, it is desirable to make a preliminary test by Wichmann's method, followed, in the case of negative results, by the evaporation directly of the original ether extract obtained by the official method, or whether it is preferable to proceed in all cases according to the complete official method, without the preliminary examination according to Wichmann.

The results reported were as follows:

Wichmann's qualitative test for coumarin.

COLLABORATOR	PURE VANILLA EXTRACT	VANILLA EXTRACT WITH 0.01 PER CENT COUMARIN ADDED
E. H. Berry, Chicago, Ill.	negative	positive
H. C. Fuller, Washington, D. C.	do	negative
A. W. Hanson, Kansas City, Mo.	do	positive
H. A. Halverson, St. Paul, Minn.	do	do
P. W. Holtzendorf, Memphis, Tenn.	do	do
W. B. D. Penniman, Baltimore, Md.	do	do
S. H. Ross, Omaha, Nebr.	do	do
A. Valin, Ottawa, Can.	do	do
	do	do
H. E. Woodward, Philadelphia, Pa.	do	negative
	do	positive
B. B. Wright, New York, N. Y.	do	negative
H. J. Wichmann, Denver, Colo.	do	positive

The following comments were made by collaborators as to the desirability of applying Wichmann's test preliminary to the official examination:

E. H. Berry: Very little time will be saved by Wichmann's method.

H. C. Fuller: Inadvisable to make preliminary test by Wichmann's method.

A. W. Hanson: Not much advantage in making preliminary test by the Wichmann method. There might be, if combined with Folin's method.

H. A. Halverson: More explicit directions should be given. Preferable to proceed according to the complete official method in all cases.

P. W. Holtzendorf: I do not consider that Wichmann's method affords any saving of time, and I prefer to operate by the official methods without preliminary examination.

C. F. Jablonski: With ample time I should prefer the official method to that of Wichmann's, but the latter is nevertheless very valuable.

S. H. Ross: Wichmann's test is valuable as confirmatory evidence, but does not afford any saving of time.

H. E. Woodward: I prefer to use the complete official method.

B. B. Wright: When a hasty examination for the presence of coumarin is desired, I consider that Wichmann's method is very valuable. However, if time permitted, I should prefer the official method.

FOLIN'S COLORIMETRIC VANILLIN METHOD.

Folin's colorimetric vanillin method appeared in the *Journal of Industrial and Engineering Chemistry,* volume 4, page 670, and depends upon the color produced in a phosphomolybdic phosphotungstic acid solution, by the addition of alkali. The method appeared very desirable for mixtures which may contain substances that would interfere with the official method, such as fats and benzoic acid. Unfortunately, however, since sending out the samples it was found that various substances give positive tests with Folin's reagent. Among these might be mentioned an infusion of cocoa beans, which appears to contain 1 per cent of vanillin when examined by Folin's method. Salicylic and benzoic acids give a very slight result.

Collaborators were requested to determine vanillin by this method on the same two samples which were submitted for Wichmann's coumarin method. The vanillin contained in the two samples was the same, and was very carefully determined independently by four analysts, using the complete provisional method. The results reported by the collaborators were as follows:

Collaborators' results on vanillin by Folin's colorimetric method.

COLLABORATOR	PURE VANILLA EXTRACT		VANILLA EXTRACT WITH 0.01 PER CENT COUMARIN ADDED	
	Folin's method	Official method	Folin's method	Official method
	grams per 100 cc.	*grams per 100 cc.*	*grams per 100 cc.*	*grams per 100 cc.*
E. H. Berry, Chicago, Ill.	0.19	0.19	0.20	0.20
H. C. Fuller, Washington, D. C.	0.20	....	0.20	....
A. W. Hanson, Kansas City, Mo.	0.18	....	0.18	....
H. A. Halverson, St. Paul, Minn.	0.20	....	0.21	....
P. W. Holtzendorf, Memphis, Tenn.	0.22	....	0.21	....
C. F. Jablonski, New York, N. Y.	0.19	....	0.19	....
A. E. Paul, Chicago, Ill.	....	0.20	....	0.20
W. B. D. Penniman, Baltimore, Md.	0.20	....	0.21	....
S. H. Ross, Omaha, Nebr.	0.20	....	0.20	....
B. H. Smith, Boston, Mass.	0.22	....	0.25	....
A. Valin, Ottawa, Can.	0.19	....	0.19	....
H. J. Wichmann, Denver, Colo.	0.22	0.20	0.22	0.20
H. E. Woodward, Philadelphia, Pa.	0.21	....	0.21	....
B. B. Wright, New York, N. Y.	0.20	0.18	0.20	0.19

The agreements and accuracy of these results, for a colorimetric process, are truly remarkable, and the method warrants further very careful study, with a view to determining its utility for extracts prepared by various methods, and in the presence of various possible interfering substances, for the purpose of testing its desirability as a method to be applied in special cases where the complete official method is not desired, or for confirmatory purposes.

PEPPERMINT EXTRACT.

Last year's referee recommended that methods for the examination of ginger and other flavoring extracts be made the subject of future work. It appeared that a method for peppermint extract was especially needed, since the provisional method has been recommended for further study.

The available proposed methods are all modifications of the precipitation method, originally devised by Mitchell for lemon extract.

HORTVET'S MODIFICATIONS.

In the modifications by Julius Hortvet brine is used for rendering the oil less soluble in the dilute alcoholic liquid. The method, as originally proposed, in the *Journal of Industrial and Engineering Chemistry*, Vol. 1, 1909, of floating the oil directly on brine, was carefully tried, and found to yield much too low results with extracts containing a low percentage of oil, but too high results for extracts containing a high percentage of oil. The reason for the low results on low grade extracts is the solubility of the oil in the alcohol-brine mixture. The explanation of the high results in high grade extracts is that the salt reduces the solubility of the alcohol in the water, so that part of it is taken up by the oil. In other words, the alcohol is partly salted out.

Hortvet later modified the method further[1] with a view of overcoming this salting out effect by drawing off the alcohol-brine solution, either by means of a finely-drawn-out tube, or from the bottom of a specially constructed bottle. But this improvement was not suggested until after the samples and methods had been submitted to the collaborators. It was sent subsequently to a few men who were thought to be especially interested in extracts, with the request that it be tried on the peppermint extracts submitted. While only three responses were received, these were from men who have had much experience with extracts.

[1] Personal communication.

HOWARD'S MODIFICATIONS.

The modifications by C. D. Howard (Bur. Chem. Bul. 137, p. 76, and *J. Ind. Eng. Chem.*, 1911, **3**: 252) depend on the removal of the oil from the diluted extracts by means of a volatile solvent, which latter is removed before centrifuging. The original method, though provisional, was recommended for study, two years ago, and it, and the further modification suggested by its author were tried by the referee, with quite satisfactory results. It appeared that some of the previously reported discordant results may be due largely to inexperience on the part of the operators. It was thought that two procedures might be advantageously combined and very slightly altered, so as to make an accurate, safe, and quick method.

The modification consists practically of the provisional method, carbon-disulphid being, however, substituted for chloroform and ether. The reason for substituting this solvent is that while its boiling point is higher than that of ether, it is much lower than that of chloroform. The details for removing the solvent are those of Howard's later modification.

CHITTICK'S MODIFICATION.

The modification of G. H. Chittick contemplates collecting the oil, before centrifuging, in a measured quantity of nonvolatile solvent, and inferring the percentage of peppermint oil from the increase in volume or from the refractive index of the oil layer. This method was first read in the convention of American Dairy, Food, and Drug Officials during June of 1913, some time after samples had been sent to the collaborators. Its author very kindly supplied a copy in manuscript, but it was not practicable to obtain collaborative results on the method. It would hardly seem, though, that the relatively large volume of oil could be read, after the manipulation, with sufficient accuracy to yield very close results nor that the refractive indices would give more than approximate results.

The results obtained by the various collaborators on extracts prepared in the laboratory from 95 per cent alcohol and finest selection of Michigan peppermint oil, are here tabulated:

Collaborator's results on peppermint extracts.

ANALYST	EXTRACT CONTAINING 0.5 PER CENT OF OIL			EXTRACT CONTAINING 3 PER CENT OF OIL			EXTRACT CONTAINING 5 PER CENT OF OIL	
	New modification of Howard's method	Hortvet's original method	Hortvet's new modification	New modification of Howard's method	Hortvet's original method	Hortvet's new modification	Hortvet's original method	Hortvet's new modification
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. H. Berry, Chicago, Ill........	0.5	Trace	Trace	3.0	3.4 3.3 3.2	2.8	5.6	5.0
C. S. Brinton, Philadelphia, Pa..	0.7 0.5	....	......	3.2 3.0	....	......	......	......
H. C. Fuller, Washington, D. C..	0.5	......	......	3.0	......	......	......	......
A. W. Hanson, Kansas City, Mo.	0.4	......	......	3.0	......	......	......	......
H. A. Halverson, St. Paul, Minn.	0.5	0.2 0.4	0.2	3.0	3.0	3.0	5.8	5.0
N. Hendrickson, Omaha, Nebr..	0.5	......	......	3.0	......	......	......	......
P. A. Holtzendorf, Memphis, Tenn........................	0.4	......	......	3.0	......	......	......	......
C. F. Jablonski, New York, N. Y.	0.6	......	......	3.3	......	......	......	......
H. L. Lourie, New York, N. Y....	0.4 0 4	....	......	2.8 3.0	....	......	......	......
W. B. D. Penniman, Baltimore, Md.........................	0.6 0.6	....	......	3.1 3.0	....	......	......	......
S. H. Ross, Omaha, Nebr......	0.5 0.6	....	......	3.0 3.0	....	......	......	......
F. L. Shannon, Lansing, Mich..	0.6	......	......	3.1	......	......	......	......
B. H. Smith, Boston, Mass.....	0.4	......	......	2.6	......	......	......	......
A. Valin, Ottawa, Can.........	0.6 0.4	....	......	3.0 3.1	....	......	......	......
H. J. Wichmann, Denver, Colo.	0.4	none	......	3.2 3.2	3.0 3.2	....	5.8 5.4	....
H. E. Woodward, Philadelphia, Pa.........................	0.6	......	......	3.3	......	......	......	......
B. B. Wright, New York, N. Y..	0.6 0.5	....	......	3.0 3.2	....	......	......	......

The following comments were made by the collaborators:

E. H. Berry: The new modification is more satisfactory than any of the old ones. Hortvet's new method gives fair results on samples containing 1 per cent or over of oil. An ordinary Babcock bottle and a drawn out tube are not satisfactory, a little oil is bound to stick and be lost. The special bottle may overcome this, but special apparatus is objectionable.

C. S. Brinton: The results may have errors due to difficulty in reading the meniscus. The method as prepared seems more satisfactory than that submitted last year.

H. C. Fuller: I can not see any advantage in this modification over the procedure of adding salt and hydrochloric acid and reading the volume of oil separated.

A. W. Hanson: A number of determinations were tried and we were pleased in obtaining results that agreed very closely.

Julius Hortvet: I recognize the fact that my new modification, even when carried out with a special bottle, gives rather low results on extracts containing appreciably less than 1 per cent of the oil. Our experience, however, shows that good results are obtainable on average commercial extracts containing oil in amounts approximating to the standard requirements.

H. L. Lourie: These readings are to the bottom of the meniscus. Reading to the extreme top gave 0.8 and 3.4 respectively. This method does not impress me as capable of giving accurate results. If the distillation of carbon bisulphid is continued too long there is loss of peppermint, if too short a time there is contamination with bisulphid.

W. B. D. Penniman: Both Howard's method and this modification give the same results and require about the same time. Howard's modification has always given satisfactory results in this laboratory.

A. Valin: I experienced a little difficulty in telling when the carbon disulphid was wholly removed.

H. J. Wichmann: I have tried Hortvet's method and have substituted solutions of various other salts, but without success. By the use of a drawn out tube there is a possible loss through oil sticking to the tube on its withdrawal.

Lourie's objections must necessarily apply to any method depending on the removal, from the oil, of a volatile solvent. As a matter of fact, however, peppermint oil has a relatively high boiling point, and the danger of loss by volatilization is easily overestimated. Certain it is that there is ample leeway between the two dangers mentioned, to enable any operator to obtain good results with very little practice. This is shown by the results reported by the collaborators.

Hortvet's original method, which has the advantage of ease of application and of time consumed in carrying out the operation, is undoubtedly very good for extracts approaching standard strength, and will be valuable for a preliminary sorting out of a series of unknown extracts, or in cases where it is merely necessary to decide whether the products are of standard strength or not. For the determination of the actual oil content in low grade extracts, the former method is better suited, and in all cases yields results remarkably close to the truth.

RECOMMENDATIONS.

It is recommended—

(1) That the results reported herewith on known samples of vanilla extracts be submitted to the Committee on Standards, for consideration in connection with such other results as are available in establishing standards.

(2) That Folin's colorimetric vanillin method, as described in the *Journal of Industrial and Engineering Chemistry*, 1912, Volume 2, page 670, be further studied on extracts prepared in various manners, and on other products containing vanillin, especially in the presence of substances which would interfere in the provisional procedure, to test its value as a

method for use in special cases where the gravimetric process is not applicable, and for confirmatory purposes.

(3) That Wichmann's qualitative method be given further consideration in connection with Folin's method, and as a preliminary test.

(4) That the following slight modifications of Howard's method for the determination of oil in peppermint extract be adopted as a provisional method:

Pipette 10 cc. of the extract into a Babcock milk bottle, add 1 cc. of carbon disulphid, mix thoroughly, then add 25 cc. of cold water and 1 cc. of concentrated hydrochloric acid. Close the mouth of the bottle with the thumb and shake vigorously for not less than 1 minute. Whirl the bottle in a centrifuge for 6 minutes and remove all but 3 or 4 cc. of the supernatant liquid by means of a glass tube of small bore and aspiration. Connect the stem of the bottle with a filter pump, immerse the bottle in nearly boiling water, start the pump and shake gently. When the carbon disulphid is practically all removed, the oil will float entirely on the surface of the watery layer. Then shake violently and immerse in boiling water for a few seconds. On disconnecting from the filter pump no odor of carbon disulphid should be detected. Cool, fill the bottle to the neck with saturated salt solution at room temperature, centrifuge for 3 minutes and read the volume of the separated oil from the top of the meniscus. Multiply the reading by 2 to obtain the per cent of oil by volume.

THE DIRECT DETERMINATION OF VOLATILE OIL OF CLOVES BY DISTILLATION WITH STEAM.

By JULIUS HORTVET.

The difficulties attending the accurate determination of essential oil in cloves and other spices have been the subject of frequent discussions during recent years. Our present official method for spices is essentially a procedure for the determination of total and volatile ether extract, and no analyst regards the so-called volatile constituent as an accurate result for essential oil. These remarks are especially applicable to the analysis of cloves. McGill,[1] Collins,[2] and Brooks[3] have suggested modifications of the procedure and also new methods, but none of these seem to have advanced to a condition suitable for general application. The high temperature to which the total ether extract is subjected in carrying out our present method of analysis is one of the conditions which has been much criticised. It is conceivable that a temperature running as high as 110°C. may cause a loss of total ether extract considerably in excess of actual volatile oil present; the result obtained may include moisture and decomposed organic substance of unknown composition.

[1] Inland Revenue Dept., Ottawa, Can., Bul. 252.
[2] *Analysis of Ground Cloves*, Swarthmore, Pa., 1910.
[3] *The Spice Mill*, Sept., 1911.

The determination of essential oil of cloves by direct distillation with steam has been proposed, and such a method has been brought forward by Girard and Dupré. The method consists essentially in mixing a weighed amount of spice with water, subjecting to distillation, and receiving the distillate in a graduated cylinder. It is stated that the volume occupied by the essential oil which is immiscible with water and separates out can be read off and its contents roughly determined. For a more accurate determination the mixture of oil and water may be extracted with petroleum ether, the ether evaporated, the residue dried at room temperature, and weighed.

R. Reich[1] has described a procedure based on this latter method, in which he distills 10 to 20 grams of the spice in a specially-constructed apparatus which provides for the passage of the steam through the loosely-packed sample placed in a capsule intermediate between the steam generator and the condenser. The distillation is continued until 600 to 800 cc. of distillate have been collected. The distillate is transferred to a separatory funnel, saturated with common salt, and extracted with sulphuric ether or petroleum ether, the latter solvent being preferred. The time required for the distillation is said to be $1\frac{1}{2}$ to 2 hours, and the entire determination, including distillation and extraction, may possibly be completed in 3 hours' time. The principle of the method involves certain features which are attractive and which indicate a possibility of an accurate procedure for the direct determination of volatile oil in cloves. Accordingly, the method has been subjected to study, and experience has developed certain modifications which seem to constitute improvements chiefly in respect to simplicity of detail and time of carrying out a determination.

DETERMINATION OF VOLATILE OIL OF CLOVES.

Apparatus. The apparatus used is the one described for the determination of volatile acids in wine and other liquors (*J. Ind. Eng. Chem.*, 1909, **1**: 31). It consists of a 350 cc. spherical flat-bottomed flask provided with an elongated wide neck, into which is fitted a 75 cc. cylindrical-shaped flask provided with a siphon-like side tube. Into the latter flask is fitted a small funnel with a stopcock and a delivery tube with safety bulb leading to a condenser.

Procedure. Place 2 grams of the spice in the inner tube of the apparatus and add 25 cc. of a 20 per cent salt solution; place 250 cc. of a 20 per cent salt solution in the outer flask, close the apparatus, and attach to the condenser. Apply heat, leaving the side outlet tube of the outer flask open until boiling has fairly begun. Then close the outlet tube and force the current of steam through the mixture of cloves and brine in the inner tube. Continue the distillation until 225 cc. of distillate have been collected, wash the distillate into a separatory funnel with 35 cc. of sulphuric ether, shake the mixture well and allow time for a good separation. The separated ether will have a somewhat cloudy and emulsified appearance. Make 3 more ex-

[1] *Zts. Nahr. Genussm.*, 1909, **18**: 401.

tractions of the distillate, using in succession 25, 15, and 10 cc. of ether. Wash the combined ether extracts with an equal quantity of water, thereby removing the cloudy appearance of the ether; a second washing is sometimes advisable. Pass the washed ether through a dry filter and wash with a little ether into a previously weighed dish, place the dish and contents in an air oven at room temperature and allow the ether to evaporate spontaneously. When the last trace of ether has disappeared weigh the dish and contents.

Results obtained by this method, compared with results obtained by the present official method, are shown in the following tabulation:

Results on determination of volatile oil of cloves.

LABORATORY NO.	TOTAL ETHER EXTRACT	VOLATILE ETHER EXTRACT	FIXED ETHER EXTRACT	WEIGHT OF OIL RECOVERED	VOLATILE OIL	DIFFERENCES
	per cent	*per cent*	*per cent*	*grams*	*per cent*	*per cent*
1704	27.80	19.23	8.57	0.3595	17.97	−1.26
1814	25.81	18.41	7.40	0.3583	17.91	−0.50
1805	24.86	16.11	8.75	0.3129	15.64	−0.47
1818	26.87	17.73	9.14	0.3497	17.49	−0.24
1800	27.45	19.03	8.42	0.3642	18.21	−0.82
1806	23.37	15.61	7.76	0.3162	15.81	+0.20
1813	25.25	16.93	8.32	0.3339	16.69	−0.24
1803	24.05	16.02	8.03	0.2908	14.54	−1.48
1807	26.61	17.17	9.44	0.3032	15.16	−2.01
1820	25.10	17.03	8.07	0.3065	15.32	−1.71
1827	28.86	20.72	8.14	0.3752	18.76	−1.96
1830	25.75	17.80	7.95	0.3283	16.41	−1.39
1832	28.48	20.73	7.75	0.3590	17.95	−2.78
1824	26.27	17.05	9.22	0.3168	15.84	−1.21
1835	24.76	16.72	8.04	0.3168	15.84	−0.88
1840	28.54	19.93	8.61	0.3736	18.68	−1.25
1798	27.80	19.15	8.65	0.3622	18.11	−1.04
1828	25.35	16.98	8.37	0.3184	15.92	−1.06
1836	25.84	16.52	9.32	0.3038	15.19	−1.33
Maximum	28.86	20.73	9.44	0.3752	18.76	−2.78
Minimum	23.37	15.61	7.40	0.2908	14.54	−0.24

The distillation method carried out as described gives results below those obtained by the official method, the differences varying from 0.24 to 2.78 per cent. Some of the high discrepancies are accounted for by the fact that the volatile constituent of the total ether extract was accidently subjected to a heat considerably above 110°C. At any rate, it is not claimed that the results by the official method afford criteria for judging results by the method of distillation. The best check on the distillation method would consist in other determinations made by the procedure modified in various ways. Five repetitions of the method on a given sample gave results varying from 17.90 to 18.06 per cent. By continuing the distillation so as to collect distillates beyond 225 cc., measuring 100 cc., 50 cc., and 50 cc. respectively, a total gain in volatile oil was obtained

amounting to only 0.02 per cent. Further attempts to obtain a greater yield of volatile oil by further extraction of the distillate with ether were found to give no increase in the results.

The spice residue remaining in the inner tube after each determination was found to have no odor resembling that of cloves. The saturation of the distillate with salt as recommended by Reich has not been found necessary or advisable. The addition of a small amount of salt solution to the sample in the distilling tube has been found to improve the condition of distillation, maintaining the volume of material uniform throughout the entire process. An improvement in the apparatus has been effected by means of a perforated enlargement at the lower end of the inner steam delivery tube. The four or five perforations thus provided serve to break up and scatter the steam jet, thus effecting a more complete mixing and contact of steam with the spice. The rapid evaporation of the ether from the volatile oil has been found inadvisable, whether by contact with live steam or other artificial heat, a very decided loss of oil resulting from any procedure of this kind. Under various conditions this loss has been found to amount to from 0.3 to nearly 2 per cent. Furthermore, it has not been found advisable to dry the residue over sulphuric acid, the loss overnight being especially appreciable owing to the fact that the oil is taken up by the acid.

Placing the residue after complete evaporation of the ether in a calcium chlorid desiccator has been found to effect a complete removal of moisture, so far as can be judged by the appearance and other properties of the residue in the flask. A number of details of this determination have yet to be worked out, but enough experience leads us to the belief that a determination of volatile oil of cloves by a procedure like the one which has been described is a proper method for such a determination, inasmuch as it is believed that the actual oil can be recovered in a sufficiently pure condition for weighing and moreover represents the actual volatile oil in the spice. If this method as applied to cloves proves to be satisfactory, the same procedure may be extended to other spices.

A motion made by V. K. Chesnut that two additional associate referees be appointed on medicinal plants and drugs was carried.

A resolution by L. L. Van Slyke for the appointment of a committee of three for the study of vegetable proteins was adopted.

PRESIDENT'S ADDRESS.

By G. S. Fraps.

It is the object of this address to present briefly the important recent advances made in agricultural chemistry. In so doing, it is not my intention to go back one hundred years, or fifty years, or even to the period included in the memory of the veterans of this association; but to consider only such a period as is within the memory and the experience of a youngster like myself.

Agricultural chemistry is so closely interwoven with the other sciences which have been applied to agriculture, that it is practically impossible to disentangle them. Hence to a certain extent the progress of the chemistry of agriculture is closely related to the progress of other agricultural sciences and to agricultural science, in general. The contributions of the chemist to agricultural science have been so many, so varied, and so important, that for a long time the sciences applied to agriculture have been termed "agricultural chemistry." This period is passing, and the term "agricultural chemistry" is being more restricted in its significance, but the field is still broad, and the harvest bountiful to the worker who seeks to garner the grain of knowledge.

There has been a tendency in some colleges to discontinue the teaching of agricultural chemistry, and to divide the subject matter between the agronomist and the animal husbandman. It is a serious question whether such tendency is in accord with the known laws of specilization in science. There is no doubt but that, as time goes on, the agricultural chemist must specialize more and more in one of these fields of work, but there is a difference between the specialization of the scientist in his own field, and the attempt of other branches of agricultural science to take over the work of the chemist, or the chemist to take over other branches of agricultural science. As I see it, both the agronomist and the animal husbandman have their special problems. They must have their special training in their own fields, and while this training must include some chemistry, it is not sufficient in quantity to make them into chemists.

On the other hand, the chemist must be first of all a chemist. The agricultural chemist must have knowledge of soils and animal nutrition, but he should have predominant chemical training and chemical methods of thought. The agronomist and the animal husbandman undoubtedly need the aid of the chemist in the solution of their problems, but they should not seek, at one and the same time, to be both agronomist and chemist. The result of such an effort is either an agronomical chemist, or a chemical agronomist. It often results in the chemist becoming also the agronomist. What agricultural science needs is the highly-trained agronomist, working, where needs be, in coöperation with a highly-trained

chemist who has perhaps specialized in soils and fertilizer chemistry, each assisting and aiding the other.

The same is true of the animal husbandman. We need the animal husbandman, highly-trained in his field and with a full knowledge of its peculiar problems, working in coöperation with the agricultural chemist, highly specialized in the chemistry of animal nutrition. In this way, we shall avoid those errors which we so often see when a man enters into a field outside of his special training—errors which the specialist immediately recognizes. The truth of the matter is, that the chemist has made such great contributions to the field of agricultural science, that the agronomist and the animal husbandman have, in many cases, not been able to see their own peculiar problems, but have emphasized the chemical side of the subject. They have not wholly found themselves. In some institutions, agricultural chemistry is no longer taught. This, we believe, is a mistake. The student needs a thorough grounding in the entire field, such as is given by the agricultural chemist, and he needs to look at agriculture, for a time, from the point of view of the chemist. Specialization should come later.

These matters will adjust themselves in time. We need not fear that the science of agriculture will ever be without the need of the agricultural chemist. Our ranks have not thinned, but each step of progress has rather added to our numbers. The Adams Act of March 16, 1906, for example, which is one of the most important events in the recent history of agricultural science, has increased the number of agricultural chemists, as well as the number of other agricultural investigators.

This act is important, not only because it increased the number of scientific agricultural workers in the experiment stations and their facilities for investigation, but because it affords to the experiment stations opportunity for fundamental research work. The passage of the Adams Act indeed marked an epoch in the history of agricultural science. The experiment stations had previously done much valuable work, and accumulated much data, a fact which the passage of the Adams Act itself recognizes, but they had such large demands upon them for immediate and practical information, that they had little time for the investigation of fundamental things, which are no less practical in their final application, but require more time and patience, and are less obvious in their practical applications. Under this act, the experiment stations not only may, but must, conduct research. Fundamental and continuous work may be done upon projects which have no present popular appeal, though no one can predict the ultimate effect of such work. The result of the Adams Act has been an increase in personnel and in facilities, and has aided in creating a demand for more highly-trained, research assistants. It has also tended to raise the standard of scientific publications of the stations. Thus, with the passage of the Adams Act, the experiment stations entered

upon a new period of their existence, one in which fundamental research becomes a much greater part of their work than has been the case in the past.

It is true that some directors of stations, and some governing boards, do not yet understand the true significance of research, or the qualifications necessary to pursue it. It is true that some station men do not, in their publications, give proper reference to previous work, which may have anticipated their own. It is true that in bulletins and reports of directors, we sometimes find claims of credit for work which are exaggerated or perhaps the credit belongs elsewhere, claims which are hardly pardonable, even after making all possible allowance for naturally exaggerated opinions of one's own work. Such things will pass away. We need more criticism of our agricultural publications—not destructive criticism, but friendly criticism, and friendly controversies over disputed points. Criticism of the proper kind is a stimulant to good work, and aids in pruning away excrescences such as those mentioned.

The Adams Act created a demand for men capable of research in agricultural chemistry, and other lines of agricultural science. Research is not an ordinary qualification, even in young men just graduated from college. The ability to do research work must be founded upon a natural ability and inclination toward such work, developed by broad general training and wide knowledge of some particular science, and by an apprenticeship under one who is himself a master of research. This apprenticeship may be during a course of work and study for the degree of Doctor of Philosophy; but it may also be in the process of regular station work under some eminent station investigator. We must recognize the fact that all men capable of research have not been able to secure the doctor's degree, even though they have done equivalent work. The ability to do research work may be developed by study and training, but it can not be created.

The Adams Act thus marks an important step in the progress of agricultural chemistry, other agricultural sciences, and agriculture as a whole. Perhaps equally as significant was the passage of the National Food and Drugs Act, approved June 30, 1906. Taken in a broad way, the passage of this act was one of a series of events in the reaction of the people against dishonest commercial practices. It has become evident that the people will no longer tolerate practices which have crept into use, which are morally wrong, but were formerly considered as all right because they were business; practices which deceive the buyer or give unfair advantages in business competition. Business has been a species of warfare, but just as it is now contrary to the laws of civilized warfare to kill women and children, and burn private dwellings, so it is becoming contrary to the laws of business warfare to cheat women and children, and to deceive the

purchaser as far as possible. How much the agitation for the pure food and drug law had to do with this moral awakening, no one can say, but no doubt this crusade of twenty-two years had much to do with it—a crusade by an agricultural chemist, Dr. Harvey W. Wiley, for many years chief of the Bureau of Chemistry, secretary of the Association of Official Chemists from its organization until only a little more than a year ago, now our honorary president—for whom all of us have a warm place in our hearts.

The Food and Drugs Act has resulted in a material clearing of the atmosphere with respect to the naming, labeling, and adulteration of foods, drugs, and feeds. We now have very clearly defined the objects of such a law. These are, first, to prevent the sale of any unwholesome or deleterious substance, and second, to ensure that the goods delivered to the purchaser shall be exactly as represented. These principles have been made clear, not only with respect to foods and drugs, but also with respect to feeds, and feed manufacturers are beginning to realize that a mixture of bran and screenings may no longer be sold as bran, or a mixture of corn bran and corn chops, sold as corn chops. There are some feed manufacturers who have not yet read aright the signs of the times, as, for example, some of the manufacturers of cottonseed meal, who contend for the authority to sell a mixture of meal and hulls under the name of cottonseed meal, but undoubtedly the time will come when this matter will be made clear.

This association has played an important part with respect to food adulteration. Before 1900, there was one referee and one associate on this subject. At the 1900 meeting, provision was made for 14 associate referees, and there are now 21 associate referees. In addition, we have our Committee on Food Standards, which has done valuable work.

In the matter of cattle feeds, their analysis and adulteration, it appears this association has done little in recent years. The analysis and control of these feeds are yearly assuming a greater importance. There should be a referee and an associate referee on the adulteration of feeds and the detection of adulterants. We have no official methods on this phase of the subject, beyond the ordinary analysis. The method for crude fiber should be thoroughly studied, and perhaps modified. The clause which permits filtration through cloth should be eliminated. The estimation of crude fiber is becoming more and more important, for by its use we can detect more easily the addition of materials rich in crude fiber, to concentrated feeds. The estimation of crude fiber, for example, shows much more clearly the probable quantity of cottonseed hulls in cottonseed meal, or of rice hulls in rice bran, than does any estimation of protein and fat.

Striking progress has been made in recent years in the survey and mapping of soils. In this work, the Bureau of Soils is easily the leader.

There is a tendency in some quarters to regard the survey, mapping, and analysis of soils as an end in itself. It is true that such work is highly important, but it should also be regarded as a basis on which to make further soil investigation, so that we may become fully familiar with the properties and characteristics of each type. In a sense, the soil survey should be regarded as the beginning of soil studies.

In other respects, our knowledge of soils has been increased by recent investigations. We now know more concerning the nature and constituents of the organic matter of the soil, and something more concerning its biological properties. We also know that, on an average, the needs of the soil for fertilizer nitrogen in pot experiments is related to the total nitrogen of the soil. We know that the active potash of the soil is related to the average needs of the soil for potash in pot experiments, and that plants have the power to exhaust the active potash, and to take up more potash than they need. We know that, on an average, the active phosphoric acid of the soil is related to the needs of the soil for phosphoric acid in pot experiments. The relation of the pot experiments, and the analysis, to field needs, must be worked out. Soils also deviate from the average, as regards their plant food content and behavior to pot experiments; such deviations must be studied, and their causes ascertained. There is much to be done, but progress is being made.

In the field of animal chemistry, decided progress has been made in recent years. We must now recognize the possibility that, in digestion, proteins of different kinds may be split into different products, some of which may be unfit for use as structural material in building up animal proteins, and so must be discarded. We know that this is possible, but we have not yet secured positive evidence that such occurs with any of the various proteins fed to domestic animals. Such studies may be expected in the future.

It has been shown, without doubt, that the digested material of different feeds have different values to the animals. One pound of digestible nitrogen-free extract in corn, has a much greater value than one pound of digestible nitrogen-free extract in straw. The fact that there is a difference in the value of the digested nutrients of the same class but from different feeds has been clearly shown by the work of Kellner and of Armsby. There is no doubt about it. It is a step forward to recognize the differences in the values of the digested nutrients, and to adjust our tables, our rations, and our calculations accordingly. There is abundant room for work along this line, but enough work has already been done to justify this advance. Nearly every American book which deals with the feeding of animals still assumes that the digestible nutrients of one feed are equal in nutritive value, pound for pound, to the digestible nutrients of the same class in any other feed. These books must be rewritten, and

adjusted to our latest advances in knowledge. This advance will, to a certain extent, reconcile these discrepancies between the effects of feeds or of rations in feeding experiments which, under the old standards, should have apparently the same nutritive values.

We are now able to state the nutritive value of a feed in terms of three factors; its bulk, which satisfies the hunger of the animal; its proteins, which repair flesh or tissue, or which, in excess, may be used for fat or energy; its fat-producing value, which is its ability to furnish the animal with heat or energy or to form fat. The fat-producing value of a feed or nutrient is determined experimentally. First, the fattening animal is fed a ration which produces a slight gain of fat, and the gain of fat is measured by determining the income and outgo of carbon and nitrogen. Next, the nutrient of feed is added to this ration. and the gain in fat again determined. The difference in the quantity of fat produced is due to the added feed or nutrient.

The results of such work may be readily compared with calculations based on the assumed equality of the same group of nutrients in different feeds. While the calculated value of peanut meal or linseed meal is practically equal to that found, the value for a wheat straw is only 20 per cent of that calculated, of meadow hay 54 per cent, of rye bran 79 per cent of that calculated.

It should be clear that the recent advances in the chemistry of animal nutrition, compel us to modify materially tables of feeding values, rations, and methods of calculations. There is opportunity for useful and valuable work along the lines of determining exactly the productive values of feeds and nutrients, and such work may be expected in the future.

In the thirteen years of the twentieth century, the progress of agricultural chemistry has been such as to satisfy even the pessimist that we are moving forward. Our facilities for scientific investigation have been increased by the Adams Act. Our supervision over foods, drugs, and feeds has been enlarged and rendered more effective through the Federal Food and Drugs Act. We have made great progress in the survey and mapping of soils, and in our knowledge of their properties and chemical composition. The science of animal nutrition has made such advances as to render it necessary to revise almost all books dealing with the subject and to modify our methods of stating the nutritive value of feeds and our methods of calculating rations for feeding animals. These have been the four chief lines of advance of agricultural chemistry in recent years. The members of the Association of Official Agricultural Chemists may well take pride in the part they have taken in the progress that has been made.

The Association adjourned until 2 p.m.

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PROCEEDINGS OF THE THIRTIETH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1913.

SECOND DAY.

TUESDAY—AFTERNOON SESSION.

W. A. Withers, chairman of the committee appointed to convey an invitation to the Secretary and Assistant Secretary of Agriculture to address the association, reported that previous engagements would prevent the Secretary from accepting but that the Assistant Secretary hoped to be at the meeting Wednesday morning. Later engagements prevented the Assistant Secretary also from speaking.

The following resolutions, offered by E. F. Ladd, were passed by the association:

Resolved, That the president and executive committee of this association memorialize the President and Congress of the United States to enact legislation authorizing the Secretary of Agriculture to establish definitions for the better enforcement of the food and drugs act of June 30, 1906.

Resolved, That the president and executive committee of the association be instructed and authorized to appoint a committee of three on definitions to coöperate with a like committee of three already appointed by the American Food and Drug Commissioners.

The members of the committee were announced later as follows: William Frear, State College, Pa., Julius Hortvet, St. Paul, Minn., and J. P. Street, New Haven, Conn.

R. W. Thatcher made the suggestion that a ten-minute limit be placed on the reading of all papers thereafter during the convention and the chair so ordered.

R. N. Brackett reported for the executive committee the following resolution:

Resolved, That the incoming president shall appoint a committee of three to contract with a responsible publisher to publish the Proceedings of the association; a definite number of copies to be contracted for and to be furnished to the Association at a reduced price.

This resolution was adopted by the association with the following supplementary motion by William Frear:

Resolved, That should the said committee of publications find the method outlined by the executive committee to be impracticable, they be further authorized to adopt such other means as in their judgment shall be best for the accomplishment of the end.

REPORT ON MEAT AND FISH.

By W. B. Smith, *Associate Referee.*

STARCH.

The methods offered to the association last year were studied comparatively this year. They are as follows:

PRICE METHOD.

Treat in a 200 cc. beaker 10 grams of finely-divided meat with 75 cc. of an 8 per cent solution of potassium hydroxid in 95 per cent alcohol, and heat on the steam bath until all the meat is dissolved. This will take from 30 to 45 minutes. Add an equal volume of 95 per cent alcohol, cool, and allow to stand at least 1 hour. Filter by suction through a thin layer of asbestos in a Gooch crucible or through an alundum crucible. Wash twice with warm 4 per cent potassium hydroxid in 50 per cent alcohol and then twice with warm 50 per cent alcohol. Endeavor to retain as much of the precipitate as possible in the beaker until the last washing. Place the crucible with contents in the original beaker, add 40 cc. of water and 25 cc. of concentrated sulphuric acid. Stir during the addition of the acid and see that the acid comes in contact with all the precipitate. Allow to stand about 5 minutes, add 40 cc. of water, and heat just to boiling, stirring constantly. Transfer the solution to a 500 cc. graduated flask, add 2 cc. of a 20 per cent aqueous solution of phosphotungstic acid, allow to cool to room temperature, and make up to mark with distilled water. Filter through a starch-free paper and after neutralizing determine the dextrose present in a 50 cc. portion of the filtrate with Fehling's solution, using Low's method, Bulletin 107, Revised, page 241, for the determination of the copper in the cuprous oxid precipitate. Dextrose $\times$ 0.9 = starch.

MAYRHOFER-SACHSSE METHOD OF E. M. BAILEY.

Treat 20 grams of the sample in a casserole with 50 cc. of 8 per cent solution of potassium hydroxid and digest on a steam bath with frequent stirring until the meat is entirely dissolved. Maintain the original volume approximately by the addition of water in case the solution concentrates appreciably. Add an equal volume of 95 per cent alcohol, stir thoroughly and filter on a small Büchner funnel provided with a thin asbestos mat. Should the filter clog and become slow, transfer the mat with residue to the casserole, removing any adhering residue in the funnel by means of a wisp of asbestos. Prepare a new filter. Add warm 4 per cent potassium hydroxid in 50 per cent alcohol to the residue in the casserole, disintegrate the mass by stirring and pour upon the new filter. Wash twice with warm 4 per cent alcoholic potash and finally with 50 per cent alcohol. (A new mat is not always necessary, but on the whole it wastes no time as the second filtration is always rapid. Moreover, the starch becomes incorporated with the asbestos and is better acted upon in the hydrolysis). Remove the filter to a 500 cc. flask, add 200 cc. of water, 20 cc. hydrochloric acid (specific gravity 1.125), and hydrolyze in a boiling water bath for two and one-half hours.. Nearly neutralize with dilute sodium hydroxid, cool, and make up to 500 cc. Determine dextrose in 25 cc. of the filtrate (equivalent to 1 gram of material), using Allihn's copper solution. Multiply the weight of dextrose by 0.9 to obtain the weight of starch.

The chemists who reported results on this work did some very thorough testing of the methods. Their reports follow:

REPORTS OF ANALYSTS.

E. A. Boyer, South Omaha, Nebr.: A sample of cornstarch designated as c.p. was used in the determinations. The anhydrous substance was found to contain 90.5 per cent of starch by the diastase method. From a closed weighing flask and weighing by difference, quantities of the starch were added to chopped fresh lean beef.

Comparison of results by methods for starch (Boyer).

PRICE METHOD		MAYRHOFER-SACHSSE METHOD	
Starch added	Starch found	Starch added	Starch found
per cent	*per cent*	*per cent*	*per cent*
1.48	1.46	1.79	1.65
2.44	2.47	1.94	1.77
4.04	3.91	3.62	3.31
4.18	4.08	3.83	3.39
4.84	4.82	4.85	4.82
5.54	5.35	6.80	5.95

Since the fundamental principles of the two methods are nearly identical, results of equal value would be expected, but for possible errors in the manipulation. With the Mayrhofer-Sachsse method trouble was experienced in the filtering and the removal of the last traces of gelatinous starch from the casserole proved extremely difficult and time-consuming. The somewhat erratic results obtained by the method are attributed to these sources. As indicated by the tabulated data the Price method proved to be an extremely accurate one for the purpose, and no difficulty was presented in the manipulation. The rapid means of digestion, lack of necessity of transferring all the starch precipitate to the filter, and the short time required for hydrolyzation are commendable points in the method. Regarding the determination of dextrose, it would appear that this might be left optional, as results here obtained have shown that the cuprous oxid precipitate is nearly free from both organic and mineral matter, and, therefore, the gravimetric methods of weighing either as cuprous oxid or cupric oxid give results nearly identical with the volumetric Low method. In laboratories making the determination frequently, possibly the Low method is preferable; if only an occasional determination of this kind is required, however, the making and standardization of the reagents necessary for conducting the volumetric method are to be considered.

Using the Price method the following figures are offered from a number showing concordant results, to show results obtained by weighing the copper either as cuprous oxid or cupric oxid, in comparison with estimating the copper by the Low method.

Starch results using cuprous and cupric oxids and Low method.

SAMPLE	PER CENT STARCH		
	Cuprous oxid	Cupric oxid	Low method
Meat food product........	4.04	3.99	3.99
do	2.54	2.52	2.51
do	3.70	3.69	3.69
do	2.96	2.92	2.92
Corn flour................	70.09	69.67	69.89
do	70.74	70.10	69.90
do	66.85	66.85	66.90

W. B. Meyer, Washington, D. C.: A comparison of the two methods shows that the Price method is much simpler in manipulation, is less liable to error, consumes less time, and gives more accurate results than the Mayrhofer-Sachsse method. With the latter, using aqueous potash to dissolve the meat, the starch is precipitated in a form that is bulky and hard to filter, a single sample requiring sometimes as much as 3 hours in spite of all the precautions suggested in the method. Error is likely to creep in when this precipitate must be transferred to a flask and difficulty is sometimes experienced in washing the precipitate from the sides of the beaker and funnel. The length of time taken for hydrolysis, 2½ hours, is another objection to the method. The Price method permits filtering the starch on an average of 10 minutes per sample. The precipitate is compact and may be filtered through a Gooch crucible, which may be put directly into the beaker which is used for digestion, and the hydrolysis conducted in about 20 minutes' time without a single transference.

Determination of starch (Meyer).

PRICE METHOD		MAYRHOFER-SACHSSE METHOD	
Starch added	Starch found	Starch added	Starch found
per cent	*per cent*	*per cent*	*per cent*
4.01	3.96	1.01	1.27
8.01	7.88	2.50	2.73
10.02	9.68	4.51	4.82
7.28	7.04	6.16	6.50
8.62	8.56	5.75	6.25
5.00	4.89	6.00	6.42
4.00	3.97	2.60	2.60
3.00	3.05	2.50	2.60
3.20	3.24	3.55	3.44
4.20	4.10	2.85	2.66
6.20	6.18	0.36	0.10
....	....	0.75	0.66

J. C. Himes, Washington, D. C.: The Price method is far superior to the Mayrhofer-Sachsse method from the standpoint of time consumed in making analyses, and the work is not tedious with the former, as it is with the latter method. I found it almost impossible to do the filtering required by the Mayrhofer-Sachsse method.

Determination of starch (Himes).

PRICE METHOD		MAYRHOFER-SACHSSE METHOD	
Starch added	Starch found	Starch added	Starch found
per cent	*per cent*	*per cent*	*per cent*
2.00	2.17	2.01	1.96
5.00	5.07	1.98	2.00
8.20	7.97	1.90	1.84
10.00	9.90	5.04	5.18
9.00	8.74	3.10	3.40
1.00	0.86	2.60	2.64
2.08	2.12	9.00	8.95
5.03	4.99	0.50	0.38
10.00	9.93	1.03	0.71
0.50	0.50	1.75	1.50
....	....	1.24	0.93
....	....	2.50	1.89

W. B. Smith, Kansas City, Mo.: The methods being so much alike it becomes a question chiefly of ease of operation. A sample of sausage gave the following results:

Starch

Price method Per cent	*Mayrhofer-Sachsse method* Per cent
2.77	2.65
2.79	2.63

The lower figures in the Mayrhofer-Sachsse method are probably due to loss of starch. This method is far more tedious and hardly as accurate as the other.

CONCLUSIONS OF ASSOCIATE REFEREE.

There is little to add to the statements of the analysts quoted. Both methods depend on the same principles, but the Price method is superior in point of time, in manipulation, and in accuracy. In the three series of tests given above the difference between starch added and found are as follows:

	Price method	*Mayrhofer-Sachsse method*
Maximum	0.26	0.85
Minimum	0.00	0.00
Average	0.10	0.23

The Price method is being used in the routine examination of thousands of samples of meat food products with unvarying success. Duplicates are found to run very closely.

AMMONIACAL NITROGEN.

The Folin method for ammonia in meats was approved last year for final action in 1913. The accuracy of the method was unquestioned, but the time and apparatus required under the form of the method used, which was that employed by M. E. Pennington for chicken flesh, and the foaming in some instances, made further study desirable.

There was also approved for study a method of distillation in alcoholic vapor. During the year, however, Folin sent the associate referee an improved form of his method, which has since been published in the *Journal of Industrial and Engineering Chemistry.* This revision is particularly adapted to meats, and while little coöperative work has been done on it, the work reported last year covered the subject so thoroughly that there seems no reason why the revised method should not be adopted.

The principles on which revision has depended are (1) the volume of the sample should be as small as possible in order to complete the operation (evolution of ammonia) quickly; (2) the sample solution should be saturated for the same reason (this is accomplished by the use of potassium oxalate); (3) the foaming complained of may be obviated, as was originally stated by Folin in 1903, by adding heavy petroleum.

The associate referee obtained the following results with the Folin-Pennington method (as recommended last year), the alcoholic vapor method, and the new Folin method:

Comparison of results by methods for ammoniacal nitrogen.

SAMPLE	AMMONIACAL NITROGEN		
	Alcoholic vapor method	Folin-Pennington method	New Folin method
	per cent	*per cent*	*per cent*
Potted meat........	0.01070	....	0.0105 0.0104
Meat extract.......	0.24400	0.25400	......
do	0.23000	....	0.2300 0.2300 0.2100 0.2200
Witte's peptone.....	0.07000 0.07700	0.04900	......
Urea	0.01700 0.02100	0.00100	......
Eggs...............	0.00450 0.00410	0.00280 0.00270	......
do	0.00182	0.00078	......

The samples of meat and meat extract show that all three methods are accurate with these substances, but for two classes of substances, such as peptone and urea, which contain large proportions of compounds easily broken down to ammonia, and such as eggs, in which the quantity of ammonia is so small that the errors in titration and of hydrolyzation assume large proportions, the alcoholic vapor method is much less accurate than the aeration methods. And since the latest modification of the Folin method makes it as easy of operation as the alcoholic method, the Folin method seems the best possible. The method as stated below is delicate enough for ordinary purposes, but if greater sensitiveness is required a larger sample can be used. The apparatus shown herewith is not large enough for eggs.

The methods used are as follows:

ALCOHOLIC VAPOR METHOD.

Mix 25 grams of the fine sample with 5 grams of salt and 1 gram of sodium carbonate and 100 cc. of alcohol in a 500 cc. flask and pass through it a current of vapor from boiling alcohol. Distill a 200 cc. portion and titrate and then treat similarly two 100 cc. portions. The last portion should contain very little ammonia.

FOLIN-AERATION METHOD.

Arrange 5 vessels in a series as follows: (1) A bottle containing sulphuric acid with a Hopkins safety bulb, to purify the entering air; (2) a 1,000 cc. flask containing 25 grams of sample, 250 cc. of water, 5 grams of sodium chlorid, and 1 gram of sodium carbonate; alcohol may be added to prevent foaming; (3) a 250 cc.

safety flask; (4) a cylinder, fitted with a Folin absorption tube, containing tenth-normal sulphuric acid; (5) a 100 cc. safety flask.

Connect the last flask to an air pump powerful enough to draw the ammonia over into the standard acid. Alcohol may be substituted almost wholly for the water if the air current is weak. Titrate the standard acid at intervals of an hour until no more ammonia is given off. Run a blank at the same time. Methyl Red, Cochineal, or Congo Red may be used in aqueous solutions, Methyl Red or Cochineal in alcoholic.

NEW FOLIN METHOD.

Weigh out 20 grams of finely-divided meat in a 50 cc. flask; add 10 cc. of water and 10 cc. of normal hydrochloric acid; let stand a few moments with occasional shaking;

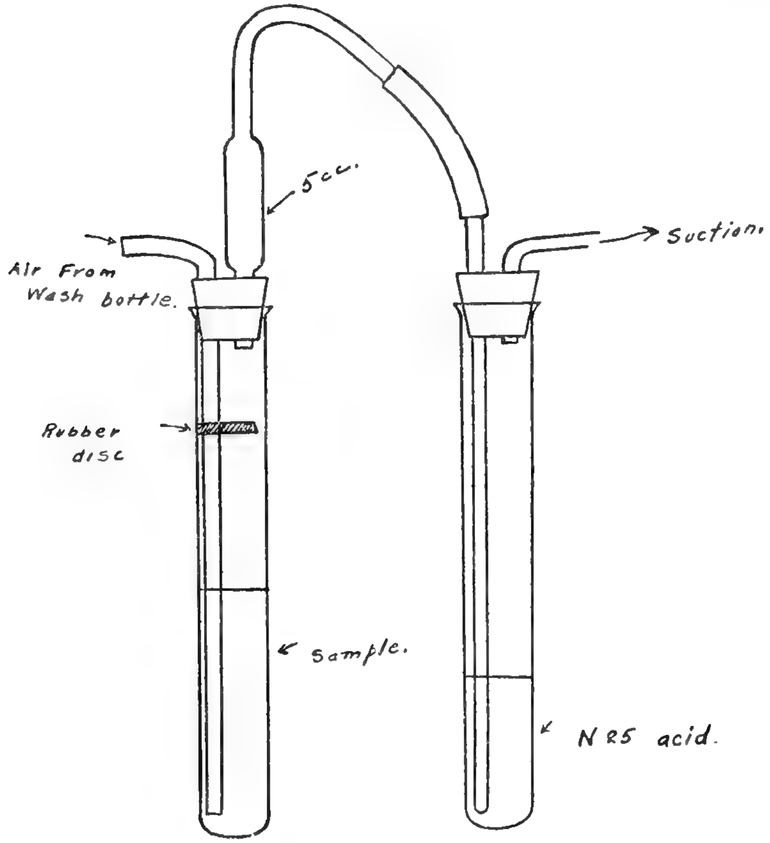

FIG. 1. APPARATUS FOR FOLIN AMMONIA METHOD.

make up to mark, and shake. Allow solid particles to settle as much as possible, pipette out 10 cc. and place in Folin apparatus shown in accompanying sketch. Place twenty-fifth-normal or fiftieth-normal acid in receiving tube and then add to the sample tube, 1 cc. of saturated potassium oxalate, a few drops of kerosene, and finally 2 cc., or enough to make alkaline, of saturated potassium carbonate.

Immediately close the apparatus and pass air, washed in sulphuric acid, through it. Collect the ammonia in the standard acid and determine its amount by titration or by Nessler's reagent.

COMMENTS OF ANALYSTS.

F. C. Weber, Washington, D. C.: We are at present using the Folin method as you describe it and consider it the best method.

F. C. Cook, Washington, D. C.: I have had some experience with the different methods and consider that the Folin method, where the amount of ammonia is determined by nesslerization preferably, and by titration, is undoubtedly the best method available at the present time for the determination of ammonia.

SUGAR.

The association voted in 1909 that the referee give special attention to the apparent error in the method for the determination of sugar in meat and meat products, noted by Lowenstein in the *Journal of the American Chemical Society*, September, 1908. This error was said to be due to the presence in the 500 cc. to which the sample was first diluted, of the insoluble portion of the 100 grams of meat taken. But the insoluble solids of meat are not enough to account for the error found. Then in well over a hundred determinations the greatest plus error ever found by the writer was 0.10 per cent, that is, 3.71 per cent were found when only 3.61 per cent were added. This may well be due to the said cause, but as in practically all cases results are low the error does not seem to be large enough to affect the results. Furthermore, the same results were obtained, whether the sugar was added before separating the solid portion or whether it was added to the filtered juice. Further discussion of this point will therefore be omitted, leaving the figures to be given to speak for themselves.

It was found, however, that the provisional method was not satisfactory for other reasons. In ordinary meats the percentage of sugar, both reducing and cane, is very small; hence it was thought necessary that a method should be found accurate to at least 0.05 per cent. The best method found in the literature appeared to be clarification with mercuric nitrate according to the description in C. A. Browne's "Handbook of Sugar Analysis," and accordingly the later work has been an effort to put this method into suitable form for meats. Mercuric nitrate alone does not remove enough of the nitrogenous bodies; for that reason phosphotungstic acid has been added with considerable success.

CLARIFICATION OF THE SUGAR SOLUTION.

Three methods were studied:

(1) *Provisional* (Bur. Chem. Bul. 107, Rev., p. 111).—Boil 100 grams of the finely-divided meat for 15 or 20 minutes in a 500 cc. graduated flask, with a convenient

volume of water. Add a few cubic centimeters of normal lead acetate, cool to room temperature, make up to mark with water, and filter through a folded filter. Remove the lead and determine reducing sugar as dextrose, as described under "VI General Methods," page 49.

(2) Same with the further addition of phosphotungstic acid.

(3) Boil 100 grams of finely-divided sample for 20 minutes with 350 cc. of water, cool, add 6 to 10 cc. of mercuric nitrate solution,[1] make to 500 cc. exclusive of fat (a graduate is convenient), and filter.

To each 100 cc. of the filtrate taken, add 1 to 2 cc. of concentrated hydrochloric acid, heat to boiling, saturate with hydrogen sulphid, remove hydrogen sulphid by a current of air, cool, add 2 cc. of 20 per cent solution of phosphotungstic acid to each 100 cc., make to same volume as taken, and filter.

Comparative results using different clarification methods, the reduction methods being comparable.

SAMPLE	REDUCING SUGAR AS DEXTROSE			
	Calculated present	Found by Method 1	Found by Method 2	Found by Method 3
	per cent	*per cent*	*per cent*	*per cent*
Sausage	2.17	1.84	1.92	2.04
	....	1.91	1.93	2.03
	....	....	....	2.11
	....	....	....	2.02
do	2.17	1.96	2.08	2.22
	....	...	....	2.28
do	4.81	4.82	....	....
Cured meat	8.00	7.90	....	....
do	4.00	4.04	....	....
do	4.00	3.62	....	....
Potted beef	3.61	3.69	3.71	....
Dried beef	2.61	2.29	2.52	....
Cured beef	1.50	1.45	1.53	....
Sausage	1.02	0.85	....	0.95
Cured ox tongue	0.92	....	0.84	....
Sausage	1.00	0.61	....	....
Cured ox tongue	0.50	0.27	0.35	....

While in the foregoing table the results by Methods 1 and 2 are in many cases good, with low percentages of sugar this is not so, the reduced copper often being held in solution or suspension by the nitrogenous bodies present, so that no precipitate is formed. The treatment with lead acetate, moreover, is not satisfactory, filtration being difficult and tedious.

Before taking up Method 3, the copper reduction will be discussed.

Only gravimetric methods have been studied, volumetric methods not appearing to have any superior advantages. Munson and Walker's

[1] Mercuric nitrate solution: Treat 220 grams of yellow oxid of mercury in 300 cc. of water with small portions of nitric acid, warm, and stir until dissolved. Make to 1,000 cc. and filter.

method, being official, has been chiefly used. This method is not so accurate when small amounts of sugar are present as with large amounts, a fact true of Allihn's also. Pflüger and Koch and Ruhsam, offer modifications of Allihn's method, chiefly consisting in boiling for 30 minutes, to overcome this, using, of course, a different table of copper values.

In cases where the cuprous oxid was precipitated clearly and red the usual Munson and Walker method was followed, the copper being determined by Low's iodid method. It sometimes happens, however, that the nitrogenous bodies still remaining in the sample solution, interfere with the reaction so that the copper is a muddy yellow. It was found that the following procedure gave practically the same ratios of copper found to sugar added as given in Munson and Walker's tables (in the columns "Copper" and "Dextrose"):

Modified Munson-Walker method of reduction.—Neutralize 50 cc. of the filtrate from the phosphotungstic acid (Method 3) with concentrated sodium hydroxid and place in a 400 cc. beaker with 25 cc. each of Soxhlet's solutions, copper and tartrate (Bur. Chem. Bul. 107, Rev., p. 42). Bring to a boil in 4 minutes and boil 2 minutes. Filter through an alundum crucible of suitable porosity (the associate referee uses some numbered 5204–RA-360) with very gentle suction. If the filtrate is green or yellow it must be refiltered until clear blue. Wash the residue with a very little 5 per cent sodium hydroxid, refiltering the washings if they are muddy. Dissolve the residue in 1 to 1 nitric acid and determine the copper by Low's iodid method (Bur. Chem. Bul. 107, Rev., p. 241). The treatment with bromin is unnecessary.

The following table shows results obtained by clarification according to Method 3 and reduction as just described, except that in some of the early experiments variations occurred. Dextrose was used in all except Experiments 4 and 5, in which cane sugar was employed. Quantitative results were obtained in both cases, showing that hydrolysis of cane sugar takes place. The lowest results given are in Experiment 2, in which too little mercuric nitrate was employed.

The difficulty of determining the blank correctly, the figure usually being low, may account for more sugar being found in some cases than was added. The average error of the above results is 0.02 per cent. Later work shows that the maximum error need not be more than 0.03 per cent. If not allowed to stand too long before filtering off the mercuric-nitrate precipitate even large amounts of starch do not cause a serious error.

Since writing the preceding part of the report comparative tests have shown that the Bertrand method of reduction, when the solutions have been properly clarified, gives the red cuprous oxid uniformly, also that the results are much less affected by the impurities present than by the

Sugar in meat by method 3.

Sample	Reagent to 500 cc. of sample		Sugar, blank on meat	Sugar added	Total sugar calculated	Sugar found
	Mercuric nitrate	Phosphotungstic acid				
	cc.	*cc.*	*per cent*	*per cent*	*per cent*	*per cent*
1—Fresh beef..........	5	Some	.....	3.00	3.00	2.92
	..	..	.....	....	....	2.98
2— do	6	10	0.07	0.98	1.05	0.99
	6	15	0.07	0.98	1.05	0.94
	6	20	0.07	0.98	1.05	0.98
Average..............	..	..	.....	....	....	0.97
	6	25	0.07	0.98	1.05	0.94
	6	30	0.07	0.98	1.05	0.93
	6	35	0.07	0.98	1.05	0.95
Average..............	..	..	.....	....	....	0.94
3—Corned beef.........	6	10	0.13	0.53	0.66	0.63
	..	..	.....	....	....	0.67
	..	..	.....	....	....	0.61
	..	..	.....	....	....	0.64
	..	..	.....	....	....	0.67
	..	..	.....	....	....	0.63
	..	..	.....	....	....	0.66
4—Summer sausage.....	6	10	0.09	0.53	0.62	0.61
	..	..	.....	....	....	0.71
	..	..	.....	....	....	0.62
	..	..	.....	....	....	0.57
	..	..	.....	....	....	0.62
5—Fresh beef.........	10	10	0.14	0.30	0.44	0.43
	10	10	0.14	0.40	0.54	0.56
	..	..	.....	....	....	0.55
	..	..	.....	....	....	0.52
	10	10	0.14	0.50	0.64	0.65
6—Sausage............	6	10	0.17	0.40	0.57	0.56
7—Cured meat.........	6	10	0.07	0.40	0.47	0.46
8—Sausage.............	5	0	0.00	0.52	0.52	0.54
	..	..	.....	....	....	0.52
	..	..	.....	....	....	0.53
	..	..	.....	....	....	0.53
9—Fresh beef.........	Some	Some	0.08	0.05	0.13	0.11
	..	..	0.08	0.10	0.18	0.17
	..	..	0.08	0.25	0.33	0.32
10—Corned beef.........	5	10	0.003	0.10	0.10	0.08
	..	..	.....	....	....	0.12
1—Sausage[1]..........	6	10	0.03	0.50	0.53	0.54
2—Fresh beef[1]..........	10	10	0.06	0.25	0.31	0.38
	10	10	0.06	0.50	0.56	0.59

[1] Results of C. T. Allcutt.

Munson and Walker method. One cause of this is the greater dilution of the solutions. The method which has given best results is as follows:

CLARIFICATION WITH MERCURY AND PHOSPHOTUNGSTIC ACID AND REDUCTION ACCORDING TO BERTRAND.

Boil 100 grams of sample with about 350 cc. of water for about 20 minutes, cool, add an excess (10 to 30 cc. of twice-normal solution) of mercuric nitrate or acetate,

nearly neutralize with sodium hydroxid, and make to 500 cc. exclusive of fat. Allow to settle and decant the clear liquid through a large folded filter without washing. Make a measured volume of the filtrate sufficiently acid (1 or 2 cc. of concentrated hydrochloric acid per 100 cc.), heat to boiling, thoroughly saturate with a rapid current of hydrogen sulphid, remove excess of hydrogen sulphid by a current of air, make to volume, and filter. Add a slight excess of 20 per cent phosphotungstic acid (in 2.5 per cent hydrochloric acid) to the filtrate, allowing for the extra volume, and place in ice-box overnight or several hours at least. Filter and determine dextrose by Bertrand's method as follows:

Make the copper sulphate solution of 40 grams to the liter, and the tartrate solution, 200 grams of Rochelle salts and 150 grams of sodium hydroxid per liter. Neutralize 20 cc. of sample with sodium hydroxid, add 20 cc. each of the copper and tartrate solutions, in a 150 cc. Erlenmeyer flask; heat to boiling and boil gently 3 minutes. Filter off the cuprous oxid, wash with water and determine copper by Low's iodid method.

A part of Bertrand's copper-dextrose table is as follows:

Mg. of copper	*Mg. of sugar*	*Mg. of copper*	*Mg. o sugar*	*Mg. of copper*	*Mg. of sugar*	*Mg. of copper*	*Mg. of sugar*
20.4	10	36.2	18	51.5	26	66.5	34
22.4	11	38.1	19	53.4	27	68.3	35
24.3	12	40.1	20	55.3	28	70.1	36
26.3	13	42.0	21	57.2	29	72.0	37
28.3	14	43.9	22	59.1	30	73.8	38
30.2	15	45.8	23	60.9	31	75.7	39
32.2	16	47.7	24	62.8	32	77.5	40
34.2	17	49.6	25	64.6	33	79.3	41

If the amount of copper found is less than 20.4 mg., the sugar value may be approximately calculated, or the sample may be concentrated on the water bath after neutralizing with sodium hydroxid and acidifying again with acetic acid. The former method is the easier and apparently as accurate.

RECOMMENDATIONS.

It is recommended—

(1) That under XVII, Methods for the Analysis of Meat and Meat Products on page 106 of Bulletin 107, Revised, 1. Identification of Species, 4th line, after "melting-point," "melting-point of stearin by Belfield-Emery method," be inserted. (This was adopted last year for the first time.)

(2) That the Price method be made the official method for starch in meat food products, in place of Mayrhofer's method, modified, 8, (b), (2), page 109, Bulletin 107, Revised.

(3) That the new Folin aeration method (*J. Biol. Chem.*, 1912, **11**: 493, 523, 527; *J. Ind. Eng. Chem.*, 1913, **5**: 485) be introduced as (g) Ammonia, on page 109, Bulletin 107, Revised.

(4) That under (e) Ammonia, page 115, Bulletin 107, Revised, the following be substituted: "Mix 1 gram of meat extract with 2 cc. of normal hydrochloric acid and wash into the Folin apparatus with about 5 cc. of water; proceed as under (g) Ammonia, page 109."

(5) That the mercury-phosphotungstic acid method for clarifying meat sugar solutions, with reduction according to Munson-Walker or Bertrand, be studied further.

REPORT ON FATS AND OILS.

By R. H. Kerr, *Associate Referee.*

GLYCEROL SAPONIFICATION METHOD FOR THE TITER TEST.

For the work on the glycerol saponification method for the titer test, recommended by the associate referee last year, the following instructions were sent to the collaborators selected for this part of the work:

INSTRUCTIONS TO COLLABORATORS.

Three samples are being sent you, one of cottonseed oil, one of inedible grease, and one of oleo stearin. It is requested that you determine the titer of these samples by the glycerol method and by the official method as given in Bulletin 107, Revised, page 135.

Glycerol method.—Heat to 150°C. in an 800 cc. beaker, 75 cc. of a glycerol potassium hydroxid solution, made by dissolving 25 grams of potassium hydroxid in 100 cc. of high test glycerol; then add 50 cc. of the oil or melted fat, previously filtered, if necessary, to remove foreign substances. Saponification in many cases takes place almost immediately, but heating, with frequent stirring, should be continued for 15 minutes, care being taken that the temperature does not rise much above 150°C. When the saponification is complete, as indicated by the perfectly homogeneous solution, pour the soap into an 800 cc. casserole containing about 500 cc. of nearly boiling water, carefully add 50 cc. of 30 per cent sulphuric acid, and heat the solution, with frequent stirring until the layer of fatty acids separates out perfectly clear. Transfer the fatty acids to a tall separatory funnel, wash three or four times with boiling water to remove all mineral acids, draw them off into a small beaker, and allow to stand on a steam bath until the water has settled out and they are clear. Filter into a dry beaker and heat to 150°C. on a thin asbestos plate, stirring continually with the thermometer, transfer to a titer tube, filling it to within 1 inch of the top, and take the titer as indicated in the present provisional method.

You are also requested to determine the iodin number of the fatty acids obtained by each method.

RESULTS OF COÖPERATIVE WORK.

The results reported by the collaborators are given in the following table:

Report of collaborators on methods for making the titer test.

SUBSTANCE AND COLLABORATOR	GLYCEROL SAPONIFICATION METHOD		PRESENT PROVISONAL METHOD	
	Titer	Iodin number	Titer	Iodin number
	°*C.*		°*C.*	
Cottonseed oil:				
L. B. Burnett (Bureau of Chemistry)	34.9	.....	35.1	.....
	34.9	111.5	34.8	110.8
H. C. Fuller (Institute of Industrial Research)	[1]32.7	78.00	[1]32.85	83.00
R. R. Henley (Bureau of Animal Industry)	34.35	105.06	34.3	106.92
R. H. Kerr (Bureau of Animal Industry)	34.1	107.60	34.1	107.70
Paul Rudnick (Armour and Co)	34.4	110.75	34.0	107.55
F. N. Smalley (Southern Cotton Oil Co.)	34.2	102.20	35.0	105.73
Maximum	34.9	.....	35.1	.....
Minimum	34.1	.....	34.0	.....
Average	34.4	.....	34.5	.....
Inedible grease:				
L. B. Burnett	41.5	....	....	.....
	41.6	57.2	41.5	57.5
H. C. Fuller	[1]40.0	33.0	[1]40.0	29.0
R. R. Henley	41.45	55.08	41.55	56.07
R. H. Kerr	41.2	54.88	41.2	54.34
Paul Rudnick	41.5	56.27	41.3	56.20
F. N. Smalley	41.6	50.76	41.7	53.15
Maximum	41.6	.....	41.7	.....
Minimum	41.2	.....	41.2	.....
Average	41.47	.....	41.45	.....
Oleo stearin:				
L. B. Burnett	50.9	.....	50.6	.....
	50.9	24.0	50.7	23.2
H. C. Fuller	[1]50.15	.....	[1]49.95	.....
R. R. Henley	50.65	21.79	50.7	22.90
R. H. Kerr	50.8	23.40	50.8	24.34
Paul Rudnick	50.9	23.78	50.8	22.93
F. N. Smalley	50.8	21.68	51.1	22.27
Maximum	50.9	.....	51.1	.....
Minimum	50.65	.....	50.6	.....
Average	50.8	.....	50.8	.....

[1] Not included in average.

COMMENTS.

The results appear to give the glycerol method a slight advantage over the present provisional method. In each case the maximum titer obtained by the glycerol method was lower and the minimum higher than by the present method. The averages were identical in two cases out of the three.

Paul Rudnick: Our results show that a slightly higher titer is consistently obtained by the glycerol method, this difference ranging inversely as the hardness of the fat. We are inclined to lay this to two features, one the use of alcohol in the

official method, the other the difference in the method of drying. When alcohol is used it is necessary to get rid of the last traces so as not to lower the titer of the resulting fatty acids. This commonly induces an error in the opposite direction, namely, scorching of the fat. Both dangers are entirely avoided by the glycerol method.

L. B. Burnett: Have obtained practically identical results with the two methods. Prefer the glycerol method for the following reasons: It is easier to manipulate, it is quicker, and the fatty acids are not so difficult to decompose when glycerol and potash are used for saponification.

As the results show clearly that the glycerol saponification method is accurate and reliable, and it is beyond question more rapid and convenient than the present method, I recommend that it be adopted as an official method.

EMERY METHOD FOR THE DETECTION OF BEEF FAT IN LARD.

A test was made of the Emery method with mixtures of lard and beef fat, lard and mutton fat, and lard and hydrogenated cottonseed oil. Eight samples were sent to the collaborators on this work, the composition of these being as follows:

Sample 1 Lard containing 5 per cent of beef tallow.
Sample 2 Lard containing 3 per cent of mutton stearin.
Sample 3 Lard containing 5 per cent of lard stearin.
Sample 4 Pure lard, 65 per cent; hydrogenated cottonseed oil, 15 per cent; cottonseed oil, 20 per cent.
Sample 5 Lard containing $2\frac{1}{2}$ per cent of oleo stearin.
Sample 6 Pure lard.
Sample 7 Lard containing 10 per cent of tallow.
Sample 8 Lard containing $2\frac{1}{2}$ per cent of hydrogenated cottonseed oil.

The following instructions were sent to the collaborators selected for this part of the work:

INSTRUCTIONS TO COLLABORATORS.

Eight samples are being sent you for the determination of the melting point of the stearins by the Emery method (Bureau of Animal Industry Cir. 132).

You are also requested to give your judgment as to which of these samples are pure lard and which are adulterated. In reaching a decision as to the purity or otherwise of any particular sample, you need not depend wholly upon the melting point of the crystals, but may use any other factors you consider of value in reaching a decision. In reporting your results please state, first, melting point of stearin crystals and temperature at which crystallization took place; second, judgment as to the purity of each sample, that is, whether it is a pure lard or not; third, what factors, if any, other than the melting point of the stearin crystals were taken into account in forming your judgment as to the purity or otherwise of each sample.

RESULTS OF COÖPERATIVE WORK.

The results reported by the collaborators are given in the following table:

Reports by collaborators on the Emery method for beef fat in lards.

COLLABORATOR AND SAMPLE	MELTING POINT OF CRYSTALS CRYSTALLIZED AT—			IODIN NUMBER	JUDGMENT	OBSERVATIONS
	12 °C.	16 C.	18 °C.			
	°C.	*°C.*	*°C.*			
L. B. Burnett, Bureau of Chemistry:						
1	62.0	62.2	62.6	61.4	Adulterated	
2	62.0	62.5	62.4	61.5	do	
3	62.4	63.3	64.0	63.4	Pure	
4	62.6	64.0	64.2	64.0	Suspicious	
5	62.4	62.5	62.4	62.2	Adulterated	
6	63.4	63.8	64.4	63.5	Pure	
7	60.8	61.8	61.6	60.7	Adulterated	
8	61.2	61.9	63.0	62.5	Pure	Remained at a temperature of 18°C. for 4 days before crystals were obtained.
H. S. Bailey, Bureau of Chemistry:						
1	....	62.5	63.0	...	Adulterated	
2	....	62.6	63.0	...	do	
3	...	63.9	64.8	...	do	
4	....	64.0	64.4	....	Pure (?)	Appears suspicious but has correct melting point.
5	....	62.7	63.8	....	Pure	
6	....	64.0	64.3	....	do	
7	...	62.4	62.0	....	Adulterated	
8	...	62.0	62.8	..	do	
Pure lard	....	63.9	64.0	....	Pure	
	14°C.°					
	°C.					
H. E. Woodward, Bureau of Chemistry (Philadelphia):						
1	61.9	62.2	....	....	Adulterated	
2	61.8	61.7	...	....	do	
3	63.1	63.2	....	..	Pure	
4	62 6	62.9	...	....	Adulterated	
5	62.0	61.9	...	....	do	
6	63.0	63 0	...	...	Pure	
7	61.0	61.3	...	.	Adulterated	
8	61.6	61.3	...	...	do	
Pure lard	63.4	63.7	..	...	.	
Lard stearin	62.5	63.2	..	....	...	
Tallow	57.8	57.3	....	...	...	
Oleo stearin	57.6	57.4	..	....	..	
		16°-18°C.				
I. R. Howlett, Wisconsin Dairy and Food Commission:		°C.				
1	...	62.8	....	....	Adulterated	
2	...	62.6	....	....	do	
3	...	64.2	....	....	Pure	
4	....	64.4	....	....	Adulterated	Microscopic appearance of crystals; melting point of fat.
5	...	63.2	....	....	do	
6	....	64.0	....	....	Pure	
7	....	62.3	....	....	Adulterated	Microscopic appearance of crystals.
8	....	62.4	....	....	do	do

Reports by collaborators on the Emery method for beef fat in lards—continued.

COLLABORATOR AND SAMPLE	MELTING POINT OF CRYSTALS CRYSTALLIZED AT—			IODIN NUMBER	JUDGMENT	OBSERVATIONS
	14 °C.	16°–18 °C.	18 C.			
	°C.	°C.	°C.			
R. H. Kerr, Bureau of Animal Industry:						
1	....	....	63.4	....	Adulterated	
2	....	....	62.4	....	do	
3	....	....	64.0	....	Pure	
4	....	....	64.0	....	Adulterated	Crystals while showing the melting point of lard crystals, are totally different in appearance.
5	....	....	63.4	....	do	
6	....	....	64.2	....	Pure	
7	....	....	61.8	....	Adulterated	
8	....	....	62.8	....	do	
	15°C.	17°C.	19°C.			
	°C	°C	°C			
W. B. Smith, Bureau of Animal Industry (Kansas City):						
1	....	62.7	62.8	....	Adulterated	
2	....	62.7	62.7	....	do	
3	63.9	64.0	64.1	....	Pure	
4	64.0	64.1	64.1	....	do	Had such a heavy precipitate that it seemed impossible that it could be pure but the Halphen test gave 20 per cent of cottonseed oil so this sample seems to be a mixture of lard stearin and cottonseed oil.
5	62.7	62.9	....	....	Adulterated	
6	63.8	64.0	64.1	....	Pure	
7	....	62.4	62.1	....	Adulterated	
8	....	61.7	61.5	....	do	
		17°–18°C.				
		°C.				
R. R. Henley, Bureau of Animal Industry:						
1	....	63.2	....	....	Adulterated	
2	....	62.4	....	....	do	
3	....	64.1	....	....	Pure	
4	....	64.2	....	....	Adulterated	Gave a large deposit of dull crystals totally different in appearance from those obtained in pure lard.
5	....	62.9	....	....	do	
6	....	64.0	....	....	Pure	
7	....	62.0	....	....	Adulterated	
8	...	62.2	....	....	do	

Samples 1 (lard containing 5 per cent beef tallow), 2 (lard containing 3 per cent mutton stearin), and 7 (lard containing 10 per cent beef tallow) were pronounced adulterated by all collaborators. Sample 6 (pure lard) was pronounced pure by all. Samples 5 (lard containing $2\frac{1}{2}$ per cent oleo stearin) and 8 (lard containing $2\frac{1}{2}$ per cent hydrogenated oil) were judged pure lard by one collaborator and Sample 3 (lard containing 5 per cent lard stearin) was judged adulterated by one. Sample 4, whose adulterants were so chosen and proportioned that the crystals obtained would show the normal melting point of pure lard, was reported as suspicious or adulterated by all of the collaborators. This sample gave a large mass of dull crystals, totally different in microscopic appearance from those given by lard.

These results show that the Emery method is not only a reliable method for the detection of beef fat in lard, but is also of value in the detection of other adulterants. The melting point of the crystals was depressed by all of the adulterants tested except the mixture of cottonseed oil and hydrogenated oil. In this case the lard was grossly adulterated without depressing the characteristic melting point of the stearin crystals, but its character and the character of the deposit were so changed that adulteration was suspected by all of the collaborators.

RECOMMENDATIONS.

It is recommended—

(1) That the glycerol saponification method for the titer test as given in this report be adopted as official.

(2) That the Emery method as given in Bureau of Animal Industry Circular 132 be adopted as a provisional method for the detection of beef fat and other solid fats in lard.

REPORT ON DAIRY PRODUCTS.

By Julius Hortvet, *Associate Referee.*

Following the recommendations adopted at the meeting in September, 1912, the work of the present year has been directed toward a study of the modifications of the continuous extraction method for determining fat in cream, homogenized cream, and ice cream. The work has included also comparative fat determinations by means of the Roese-Gottlieb method and an examination of the fat recovered by the continuous extraction method described by the associate referee in 1911.

The collaborators were also requested to undertake a microscopic examination of the samples submitted with a view of the possible detection of homogenization. One of the collaborators has given special attention to this feature of the work, and his report is submitted herewith.

Samples of various kinds of cream products, two of which were homogenized and two of which contained known proportions of foreign fat, were submitted to the collaborators. The samples submitted included: (1) Pure untreated sweet cream; (2) same cream homogenized; (3) same cream homogenized with oleo oil (added to constitute 20 per cent of the fat); (4) ice cream made from same cream with gelatin, sugar, and cottonseed oil (added to constitute 20 per cent of the fat). All samples were preserved with a little formaldehyde.

The plan of preparation of the samples for the fat determinations has been somewhat revised, although it differs in no essential respects from the usual procedure. The aim has been to adapt the method of preparation to the character of the samples to be extracted.

The collaborators were requested to make the following determinations upon the fat recovered from the various samples:—Reichert-Meissl number, iodin number, refractive index at 25°C.

The methods for Reichert-Meissl number and refractive index are in all essential respects as described in Bulletin 107, Revised, pages 131, 136, and 141. The method for the Reichert-Meissl number determination is essentially the Leffman and Beam method given on page 141.

The associate referee is indebted to E. H. Farrington and A. C. Baer, of the University of Wisconsin Agricultural Experiment Station, for their services in preparing these samples and forwarding them to the various collaborators.

The entire description of the methods as submitted to the collaborators is given as follows:

INSTRUCTIONS TO COLLABORATORS.

DETERMINATION OF FAT.

A—Roese-Gottlieb Method.

(*1*) *Milk* (*whole or skimmed*).—If the milk be soured, obtain an even emulsion preferably by repeatedly pouring the sample back and forth from one container to another. Unless a fine, even emulsion can be secured, it will not be expected that a satisfactory analysis can be made. Weigh out 3 to 5 grams of the homogeneous sample and transfer to a Röhrig tube (Zts. Nahr. Genussm., 1905, **9**: 531) or to a suitable size Werner-Schmidt extraction apparatus (Leach, 3d Ed., p. 139), using for the purpose not more than 10 cc. of water.

(*2*) *Evaporated milk* (*sweetened or unsweetened*) *and cream.*—Mix the sample thoroughly, best by transferring the entire contents of the can or bottle to a large evaporating dish, and working it with a pestle until homogeneous throughout. Weigh 40 grams of the prepared sample, preferably in a tared weighing dish used for sugar analysis, transfer by washing to a 100 cc. graduated sugar-flask and make up to the mark with water. Measure into one of the extraction tubes described in the preceding paragraph 10 cc. of this solution.

(*3*) *Ice cream.*—Soften the sample, by warming, to the consistency of ordinary cream, transfer to a beaker and stir until homogeneous throughout. Weigh out

3 to 5 grams of the sample, transfer to an extraction tube, using for the purpose not more than 10 cc. of water.

(*4*) *General procedure.*—To the material in the extraction tube add 1.25 cc. of concentrated ammonium hydroxid (2 cc. if the sample be sour) and mix thoroughly. Add 10 cc. of 95 per cent alcohol and mix well; add 25 cc. of washed ethyl ether, shake vigorously for a half minute, add 25 cc. of petroleum ether (redistilled slowly at a temperature below 60°C. preferably) and shake again for a half minute. Let stand 20 minutes or until the upper liquid is practically clear and its lower level constant. Draw off the ether fat solution as much as possible (usually 0.5 to 0.9 cc. will be left) into a weighed flask through a small quick-acting filter. Re-extract the liquid remaining in the tube, this time with only 15 cc. of each ether, shaking vigorously half a minute and allow to settle. Draw off the clear solution through the small filter into the same flask as before and wash the tip of the spigot, the funnel, and the filter with a few cubic centimeters of a mixture of the two ethers in equal parts. Extract again and wash in the manner just described. Evaporate the ether slowly on a steam bath, then dry the fat in a water oven until loss of weight ceases.

B—Continuous Extraction Method of A. E. Paul.

(*1*) *Milk and evaporated milk (sweetened or unsweetened) and thin ice cream.*—Prepare the material in the manner described under *A*. Into a 1,000 cc. beaker weigh 100 grams (in the case of milk 200 grams) of sample. Add 300 cc. of water, mix thoroughly and heat to boiling; add while boiling, very gradually 25 cc. of Soxhlet's copper sulphate solution diluted with 100 cc. of water. In a Büchner funnel wet a filter of suitable size and of loose texture. Filter with suction and wash three times with a little boiling water, filtering as dry as possible. Remove the cake, which should be dry enough to be broken up easily between the fingers, break into small particles, and dry in the open air overnight. Grind in a mortar with sufficient (usually 25 grams) anhydrous copper sulphate, let stand a few minutes, or until the product seems quite dry and not at all lumpy. Into the inner tube of a large Soxhlet or other extraction tube place a layer of anhydrous copper sulphate, then the powdered mixture. Place on top a loose plug of cotton and extract 16 hours with ordinary ether. The ether should be poured into the extractor and allowed to percolate through before the heating is begun. About 50 cc. of the solvent will be required. Evaporate the ether slowly on a steam bath, then dry the fat in a water oven until loss of weight ceases. Reserve the weighed fat for further examination.

(*2*) *Cream and thick ice cream.*—Prepare the material in the manner described under *A*. In a Büchner funnel wet an 11 cm. filter of loose texture and cover with a layer of fibrous asbestos, being careful to cover the sides as far up as possible. In a 250 cc. beaker boil 25 cc. of Soxhlet's copper sulphate solution, and add, while stirring vigorously, 50 grams of the material. Immediately remove the source of heat and filter with slow suction. Wash once or twice with a small amount of cold water, and proceed as in the method described for evaporated milk.

EXAMINATION OF THE FAT.

A—Reichert-Meissl Number.

(*1*) *Preparation of reagents.*—(a) Sulphuric acid—Dilute 200 cc. of the strongest acid to 1,000 cc. of water.

(b) Barium hydroxid solution—Standardize an approximately tenth-normal solution.

(c) Indicator—Dissolve 1 gram of phenolphthalein in 100 cc. of 95 per cent alcohol.

(d) Pumice stone—Heat small pieces to a white heat, plunge in water, and keep under water until used.

(e) Glycerol soda solution—Add 20 cc. of sodium hydroxid solution, prepared by dissolving 100 grams of sodium hydroxid, as free as possible from carbonates, in 100 cc. of water, to 180 cc. of pure concentrated glycerol.

(*2*) *Determination.*—Add 20 cc. of the glycerol soda to approximately 5 grams of the fat in a flask, weighed accurately, and heat over a naked flame or hot asbestos plate until complete saponification takes place, as is shown by the mixture becoming perfectly clear. If foaming occurs, shake the flask gently. Add 135 cc. of recently boiled water, drop by drop at first, to prevent foaming, and 5 cc. of the dilute sulphuric acid solution, and distill, without previous melting of the fatty acids 100 cc. in about 30 minutes. Mix this distillate, filter through a dry filter, and titrate 100 cc. with the standard barium hydroxid solution, using 0.5 cc. of phenolphthalein as indicator. The red color should remain unchanged for two or three minutes. Increase the number of cubic centimeters of tenth-normal alkali used by one-tenth, divide by the weight of fat taken, and multiply by 5 to obtain the Reichert-Meissl number. Correct the result by the figure obtained in a blank experiment.

B—Iodin Number.

(*1*) *Preparation of Reagents.*—(a) Iodin solution—Dissolve 13.2 grams of pure iodin in 1,000 cc. of pure glacial acetic (99 per cent), and to the cold solution add 3 cc. of bromin, or sufficient to practically double the halogen content when titrated against the thiosulphate solution, but with the iodin slightly in excess.

(b) Decinormal thiosulphate solution—Make by dissolving 24.6 grams of the freshly-powdered, chemically-pure salt in water, and make up to 1,000 cc.

(c) Starch paste—Prepare by boiling 1 gram of starch in 200 cc. of water for 10 minutes, then cool.

(d) Potassium iodid solution—Make by dissolving 150 grams of the salt in water, and making up the volume to 1,000 cc.

(e) Potassium bichromate solution—Make by dissolving 3.874 grams of chemically pure potassium bichromate in distilled water, and making up the volume to 1,000 cc.

(*2*) *Standardization of the thiosulphate solution.*—Introduce 20 cc. of the potassium bichromate solution into a glass-stoppered flask together with 10 cc. of potassium iodid and 5 cc. of strong hydrochloric acid. Then add slowly from a burette the sodium thiosulphate solution until the yellow color of the solution has nearly disappeared, after which add a little of the starch paste, and carefully continue the titration to just the point of disappearance of the blue color. Find the equivalent of 1 gram of iodin in terms of the thiosulphate solution by multiplying the number of cubic centimeters of the latter solution required for the titration by 5. The reciprocal of this result (expressed decimally) is the equivalent of 1 cc. of the thiosulphate solution in terms of iodin.

(*3*) *Procedure.*—Weigh out 0.3 to 0.5 gram of the fat in a glass-stoppered flask of 300 cc. capacity. Dissolve the fat in 10 cc. of chloroform, add 30 cc. of the iodin reagent, shake, and set in a dark place for half an hour. Add 10 cc. of the potassium iodid solution and 100 cc. of distilled water. Titrate the excess of iodin with the thiosulphate solution, which is slowly added from a burette until the yellow color has nearly disappeared, then add a little starch paste, and finally thiosulphate solution drop by drop until the blue color of the iodized starch is dispelled. Stopper

and shake the flask vigorously, and add sufficient thiosulphate to prevent a reappearance of the blue color in five minutes. Conduct a blank determination at the same time, in exactly the same manner as in the above in order to obtain the cubic centimeters of thiosulphate solution equivalent to the 30 cc. of iodin solution used in the determination. Calculate the percentage of iodin absorbed (Leach, 3d ed., p. 489).

C—Refractive Index at 25°C.

Take at any convenient temperature and calculate to 25°C. by the formula:

$$R = R' + 0.55\ (T' - T),$$

in which R is the reading reduced to T, R' the reading taken at temperature T' (Bulletin 107, Revised, p. 131).

RESULTS OF COÖPERATIVE WORK.

The reports of the collaborators are included in the table on pages 186 and 187.

DISCUSSION.

All collaborators report difficulty in obtaining satisfactory results on Sample 1, owing to the somewhat churned or partly-separated condition of the fat. The other samples were received in good or fairly good condition. Allowing for these difficulties, however, the results are quite satisfactory, and the consensus of opinion is that the continuous extraction method applied to rich cream and cream products will not only yield reliable quantitative results, but a sufficient amount of fat in proper condition for chemical examination. The general trend of the results indicates that the new method recovers as a rule a larger proportion of fat, both in the unhomogenized and homogenized samples. There are some irregularities which can be accounted for by lack of experience on the part of the analyst. There is sufficient evidence in the results submitted to indicate that the modified new method may be relied upon when carried out under proper conditions and by an experienced analyst. The indications are that the results for fat will be higher than results obtained by the Roese-Gottlieb method.

It is to be regretted that no reports have been received from two of the persons who offered to collaborate, and that one or two others were not able to submit complete reports.

It is shown by results that the Reichert-Meissl number is an important factor in judging the character and approximate percentage of foreign fat. The refractive index figures are very significant, especially in the case of Sample 4, and the iodin numbers on Samples 3 and 4 are decidedly corroborative of indications afforded by the Reichert-Meissl determinations.

The following comments and criticisms were made by the collaborators:

Reports of collaborators on fat determinations.

SAMPLE AND COLLABORATOR	FAT BY ROESE-GOTTLIEB METHOD	FAT BY CONTINUOUS EXTRACTION	REFRACTIVE INDEX AT 25°C.	REICHERT-MEISSL NUMBER	IODIN NUMBER	HALPHEN TEST	FOREIGN FAT INDICATED IN FAT EXTRACTED	CONDITION OF SAMPLE RECEIVED
	per cent	*per cent*						
1. Pure untreated sweet milk:								
C. H. Biesterfeld	.....	.....	....	.....	.....	....	....	Churned and lumpy
C. B. Gnadinger	13.96 14.06	13.68	1.4616 53.4	24.45	38.8 38.5	....	None	Badly separated
L. B. Burnett	13.27 13.32	15.34	1.4624 1.4622	21.60	38.69 39.01	....	....	Somewhat churned
C. C. Forward	15.03 14.95 15.11	15.04 14.48	53.7	24.85 25.0	38.5 39.0 38.45	....	....	do
G. G. Parkin	11.02	14.42 14.31	1.4607	.....	.....	....	....	....
2. Same cream as 1, homogenized:								
C. H. Biesterfeld	15.51 15.55	15.49 15.53	1.4623 54.3	24.3 24.4	38.2 38.6	....	....	....
C. B. Gnadinger	15.51 15.51	15.53 15.56	1.4617 53.6	24.20 23.20	38.5 38.7	....	None	Good
L. B. Burnett	14.45 14.60	15.58 15.52	1.4624 1.4622	22.05	37.97 38.9	....	....	....
C. C. Forward	15.39 15.00 15.29	15.46 15.48	53.5	24.7 23.7	40.05 40.65 40.00	....	....	....
G. G. Parkin	15.49	15.34	1.4605	.....	.....	....	....	....
3. Same cream as 1, homogenized with oleo oil:								
C. H. Biesterfeld	.....	.....	....	.....	.....	....	....	Broken.
C. B. Gnadinger	21.75 21.89	23.12	1.4620 54.0	15.52 15.53	39.8 39.5	....	About 35-40 per cent	Somewhat separated.
L. B. Burnett	20.30 20.00	22.29 22.18	1.4624 1.4622	14.7	39.64 42.98	....	....	....
C. C. Forward	.....	22.70 22.73	54.0	16.1 15.6	42.75 42.65	....	About ⅓ oleo oil	....
G. G. Parkin	21.82	22.34 22.27	1.4624	.....	.....	....	....	....

Reports of collaborators on fat determinations—Continued.

SAMPLE AND COLLABORATOR	FAT BY ROESE-GOTTLIEB METHOD	FAT BY CONTINUOUS EXTRACTION	REFRACTIVE INDEX AT 25°C.	REICHERT-MEISSL NUMBER	IODIN NUMBER	HALPHEN TEST	FOREIGN FAT INDICATED IN FAT EXTRACTED	CONDITION OF SAMPLE RECEIVED
	per cent	*per cent*						
4. Ice cream from 1, with gelatin, sugar and cottonseed oil:								
C. H. Biesterfeld	17.34 17.35	17.33	1.4664 61.7600	15.6	52.6	....	....	....
C. B. Gnadinger	17.34 17.19	17.29 17.26	1.4655 59.4	16.15 16.07	57.6 57.5	Positive	About 35–40 per cent	Good.
L. B. Burnett	16.52 16.66	17.28 17.26	1.4668 1.4657	14.75 14.55	63.87 64.0	....	....	....
C. C. Forward	17.55 17.42 17.18	15.63 16.97	58.8	17.2 17.0	60.2 60.25	....	About $\frac{1}{3}$ cottonseed oil.	....
G. G. Parkin	17.37 17.40	17.23 17.30	1.4680	.....	.....	....	....	....

COMMENTS OF COLLABORATORS.

C. H. Biesterfeld, Bureau of Chemistry: Results by the Paul method are fine, being practically the same as by the Roese-Gottlieb. Whether the fats suffered any by standing a month in the refrigerator, I do not know.

D. B. Gnadinger, Bureau of Chemistry (Chicago): It would seem that the continuous extraction method yields a quantitative recovery of fat, and that for most dairy products it has the advantage of calling for a larger quantity of fat, thus insuring a better average sample than can be secured by the Roese-Gottlieb method. In my estimation, therefore, the extraction method is satisfactory for both purposes; the quantitative fat determination, and the separation of sufficient fat for examination. Of the constants determined, it is my opinion that the Reichert-Meissl value is the one to be depended upon. The others may be useful for the purpose of corroboration. As to the question of homogenization, nothing was done, except to note the striking difference in the condition of the homogenized and unhomogenized samples; the former were quite smooth, and any slight separation was easily stirred up, with the result that quite a homogeneous mixture was obtained, while the latter was entirely separated.

L. B. Burnett, Bureau of Chemistry: Have obtained more consistent results with the continuous extraction method. While requiring much more time, no trouble was experienced with the method. The modification suggested for ice cream, that is, the manner of filtering on a pad of fibrous asbestos, although filtering slowly, a clear filtrate was obtained. Was considerably surprised to find that the percentage of fat as obtained with the extraction method was invariably higher than that with the Roese-Gottlieb method. As a check the nonvolatile matter was estimated in the ether used for extracting, also the extract was dissolved in petroleum ether and weighed a second time, but the corrections introduced in this way were very slight. It is suggested that there was an incomplete extraction in the Röhrig tube. A third extraction was made in the Roese-Gottlieb method in addition to the two requested, but the amount of fat obtained was so small as to be practically negligible.

C. C. Forward, Laboratory of the Inland Revenue Department, Ottawa, Can.: The results obtained by the method of A. E. Paul for fat in ice cream are not very satisfactory. If there had been more of the samples allowing for further work, results obtained might show to better advantage as the method requires some practice in manipulation in order to use it accurately. Sample 3 appears to be a mixture of butter fat with about one-third oleo oil, or about 7½ per cent oleo oil in the total mixture. In Sample 4 about one-third of the fat appears to be cottonseed oil.

G. G. Parkin, State Dairy and Food Department, St. Paul, Minn.: Some difficulty was experienced in grinding the dried material with anhydrous cupric sulphate until free from lumps. The large amount of oil or fat was probably the cause of this trouble. The tendency of the material to pack in the extraction tube afforded some trouble, which was overcome by the packing of two alternate layers of cotton and material. The continuous extraction method gave results which agreed very well with the Roese-Gottlieb method. Its application would be advisable in all cases where a large amount of oil or fat is desired for further analysis and where the time element is not to be considered.

R. W. Hilts, Bureau of Chemistry (Seattle): I have made a microscopic examination of the samples with a view of detecting homogenization. The samples were examined under a magnification of 450 diameters with a micrometer eye-piece.

Sample 1: The fat globules vary much in size. The large ones range from 5 to 9.6 microns in diameter; the medium size, which predominate, range from 3.3 to

4.1 microns, and the smallest globules about 0.2 to 0.8 micron. In this normal sample, by far the bulk of the fat exists in the middle and large size globules, leaving considerable free space apparent between them.

Sample 2: The large and medium size globules range from 2.7 to 6.9 microns in diameter and the small ones about 0.2 to 0.5 micron. In this sample the small globules predominate immensely in number, the medium and large ones being relatively few in number. The small globules are so numerous that free spaces between them are very small.

Sample 3: The large and medium globules range from 1.6 to 9.6 microns in diameter, the small ones about 0.2 to 1.3 microns. The statements made relative to Sample 2, as to general appearance and distribution of the globules, apply to this sample. There is noted in this sample, however, some very large globules that are even larger than those found in normal milk, due, doubtless, to the use of a foreign fat.

Sample 4: The large and medium globules range from 2.7 to 8.2 microns in diameter and the small ones from 0.2 to 1.3 microns. The general appearance of the sample is the same as Sample 3.

The use of a micrometer eye-piece is not necessary to distinguish the homogenized from the natural product as the relative numbers of small, medium, and large globules are very striking to the eye, using the magnification stated. The measurements given for the smallest globules are only approximations, as they are really too small for measurement. Note that Koenig states, (Chem. Mensch. Nahr. Genussm., 4th ed. **2**: 588) that the fat globules of cow's milk range from 0.2 to 10 microns in diameter, average being 2 to 3 microns.

RECOMMENDATIONS.

No further modifications of the proposed new method are suggested. It is believed that the method promises very favorably to be a valuable one, especially in view of the growing tendency to incorporate foreign fats into creams and ice creams. The results are doubtless sufficiently uniform to warrant a positive recommendation that the method be adopted as provisional at this meeting. It is also recommended that the general continuous extraction method as described in this report and the modifications for milk and cream products be given further study, especial attention to be given to the modification for rich cream and ice cream.

SUPPLEMENTAL REPORT.

By C. H. Biesterfeld.

In the work on creams by the Paul method, the mass after extraction for 16 hours was reground and re-extracted for 5 hours, yielding the amounts of fat shown below, which were in each case less than 0.02 per cent on the charge taken. These amounts were included in the results previously reported.

METHOD	SAMPLE 2			SAMPLE 4		
	Weight	Fat		Weight	Fat	
	grams	*gram*	*per cent*	*grams*	*gram*	*per cent*
Paul's method 1.........	27	0.0028	0.010	..	......	.....
Paul's method 2.........	50	0.0095	0.019	50	0.0081	0.016

W. F. Hand gave a short talk on a piece of special apparatus used in the analysis of dairy products.

A paper by H. J. Wichmann on Lime as a Neutralizer in Dairy Products was read by G. E. Patrick.

REPORT ON CEREAL PRODUCTS.

By H. L. White, *Associate Referee.*[1]

At a meeting of Committee C of this association held in 1912, the following recommendations, relative to methods for the analysis of wheat flour, were adopted:

(1) That the method of Bryan, Given and Straughn (Bur. Chem. Cir. 71) for soluble carbohydrates be given a further trial.

(2) That methods for the estimation of moisture by the use of the vacuum oven and vacuum desiccator, for estimating the acidity of the water extract of flour and Olson's method for dry gluten be referred to the next referee for immediate consideration.

SOLUBLE CARBOHYDRATES.

In following out these instructions two samples of flour were sent to each of six chemists who had offered to collaborate in the work. Sample 1592 was a hard red spring wheat patent. Sample 1244 was a straight flour made from a mixture of hard red spring wheat containing five per cent of sprouted wheat. Both samples gave good baking results, No. 1592 having a loaf volume of 2340 cc. and No. 1244 a loaf volume of 2345 cc.

METHODS AND RESULTS.

Soluble carbohydrates as dextrose.

The method of Bryan, Given, and Straughn (Bur. Chem. Cir. 71), using both sodium carbonate and alcohol for extraction gave the following results:

[1] Read by E. F. Ladd.

Comparative results on soluble carbohydrates as dextrose.

ANALYST	SAMPLE 1244		SAMPLE 1592	
	Extraction with alcohol	Extraction with sodium carbonate	Extraction with alcohol	Extraction with sodium carbonate
	per cent	*per cent*	*per cent*	*per cent*
R. F. Beard, Agricultural College, N. D.	[1]1.49	[1]1.42	[2]1.04	[1]1.56
H. O. Lichtenwalter, Kansas City, Mo.	[3]1.65 [3]1.58	....	[3]1.12 [3]1.20	....
L. H. Bailey, Washington, D. C.	[1]1.49	[1]1.99	[1]1.12	[1]1.61

[1] Average of 3 determinations. [2] Average of 4 determinations. [3] Results calculated from results expressed as invert sugar in next table.

In connection with the work on carbohydrates, Mr. Lichtenwalter sent in the following results:

SAMPLE NO.	EXTRACTION WITH ALCOHOL			EXTRACTION WITH SODIUM CARBONATE		
	Reducing sugar calculated as invert	Total sugar calculated as invert	Sucrose	Reducing sugar calculated as invert	Total sugar calculated as invert	Sucrose
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1244	0.29	1.67	1.31	0.98	1.91	0.88
	0.28	1.74	1.38	0.97	Lost	Lost
1592	0.23	1.19	0.91	0.92	1.56	0.61
	0.25	1.27	0.96	0.89	1.60	0.67

Method I.—Use official method (Bulletin 107, Revised, page 38, 1), as a check.

Method II.—Vacuum desiccator: In an eighth-inch Hempel desiccator put 1 liter of sulphuric acid (specific gravity 1.84). Weigh out 9 samples of flour of 2 grams each into tared flat aluminum dishes, fitted with covers. Exhaust the air, using a vacuum gauge to indicate the pressure. (Some workers maintain a vacuum of 1 mm.; see *J. Soc. Chem. Ind.*, 1913, **32**: 72). In other determinations a vacuum of 15 mm. was maintained (Ibid., p. 69). Thoroughly mix acid and water layer twice each day. Remove and weigh 3 samples at the end of 3 days, 3 samples at the end of 5 days, and 3 at the end of 7 days. Increase the time until constant weight is obtained.

Method III.—Vacuum oven: Using 2 gram samples of flour, make a comparison of results obtained at 70°C. and 100°C. for 5 hours, maintaining the same vacuum, preferably 60 mm.

Comparative results obtained by use of the different methods of determining moisture are given in the following table:

Comparative results on moisture.

ANALYST	METHOD I		METHOD II										METHOD III			
	Sample 1244	Sample 1592	Sample 1244					Sample 1592					Sample 1244		Sample 1592	
			3 days	5 days	6 days	7 days	9 days	3 days	5 days	6 days	7 days	9 days	5 hours	6 hours	5 hours	6 hours
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
L. H. Bailey, Washington, D. C.	[1]11.96	[1]11.80	11.99	12.14	.....	11.93	....	11.96	11.90	.....	11.89	.....	10.86	10.62	10.86	10.73
R. F. Beard, Agricultural College, N. D.	[2]12.21	[2]12.01	11.31	.....	11.99	.....	11.91	11.66	.....	12.13	.....	12.14	.....	.....	.....	.....
Average	12.08	11 90	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

[1] Approximately 85 mm. mercury pressure.
[2] Approximately 10 mm. mercury pressure.

L. H. Bailey reports that on heating Sample 1244 one hour longer than in Method I, a loss of 12.07 per cent resulted; Sample 1592 under the same conditions showed a loss of 11.90 per cent. In Method II he maintained a pressure of not more than 10 mm. of mercury with Sample 1592, and with some variation in Sample 1244. R. F. Beard began with an initial pressure of 3 mm. of mercury and re-exhausted desiccator on each day that samples were removed for weighing. At the end of the 9-day period, the pressure in the desiccator was 114 mm. of mercury. The results seem to indicate that 5 or 6 days in a vacuum desiccator under low pressure gives the maximum loss of weight. Method III was tried in vacuum oven at 70°C. and at a pressure of approximately 80 mm. of mercury. The results obtained at 70°C. are considerably lower than those obtained by other methods.

GLUTEN.

Olson method.—Dough up 10 grams of flour with 6 cc. of water. After weighing the wet gluten, place it in a vacuum oven and dry for 3 hours under 65 cm. vacuum at 85°C. The reduced pressure and the temperature combine to cause the gluten to expand rapidly. Compare the results with those obtained by the method given in Bureau of Chemistry Bulletin 122, page 54.

Comparative results on gluten.

ANALYST	SAMPLE 1244				SAMPLE 1592			
	Olson method		Bulletin 122 method		Olson method		Bulletin 122 method	
	Moist	Dry	Moist	Dry	Moist	Dry	Moist	Dry
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
R. F. Beard, Agricultural College, N. D.	33.39	14.63	...	...	34.56	13.32	...	...
H. L. Wessling, Washington, D. C.	...	10.81		10.51	...	10.95		10.85

ACIDITY OF WATER EXTRACT.

The acidity of the water extract of wheat flour depends on the time and temperature of extraction. Last year all collaborators agreed on 40°C. as being the best temperature to maintain, but disagreed on the time of extraction. It seems desirable to limit the time of extraction to two hours at the most; perhaps one hour will be more satisfactory. The method is as follows:

Method.—Weigh out 18 grams of flour into a 500 cc. Erlenmeyer flask and add 200 cc. of distilled water free from carbon dioxid. Place the flask in a water oven kept at a temperature of 40°C. for the time indicated, shaking vigorously every half hour. Filter through dry double filters, rejecting the first 10 cc. of filtrate until 100 cc.

is obtained. Titrate with twentieth-normal sodium hydroxid using carefully neutralized phenophthalein as an indicator. Each cubic centimeter of sodium hydroxid solution represents 0.05 per cent of acidity expressed as lactic acid.

Comparative results on acidity of water extract.

(Expressed as per cent of lactic acid).

ANALYST	SAMPLE 1244		SAMPLE 1592	
	1 hour	2 hours	1 hour	2 hours
H. L. Wessling, Washington, D. C.[1]	0.125	0.130	0.135	0.145
H. L. White, Agricultural College, N. D.	0.128	0.146	0.130	0.155

[1] Used 2 cc. of phenolphthalein as indicator.

RECOMMENDATIONS.

It is recommended—

(1) That the method of Bryan, Given and Straughn for the estimation of soluble carbohydrates be made official (results to be expressed as dextrose).

(2) That the method for the estimation of acidity of water extract of flour given in this report, be made official.

REPORT ON VEGETABLES.

By E. W. Magruder, *Associate Referee.*

CANNED FOODS.

Since the associate referee for 1912 made no recommendations, it was decided to make some study of the percentage of easily separable liquid in some canned foods, such as tomatoes, corn, and butter beans. Time for this work, however, was limited and canned tomatoes was the only product studied.

After some experimenting the regular fertilizer sieve with round holes 1 mm. in diameter was adopted as the best for separating the liquid from the solid portion. The method of procedure was as follows:

Determine the weight of the contents of the can and then transfer the material to the sieve and stir the material gently with a spatula to allow the liquid to drain away; allow the material to remain on the sieve 5 minutes, gently stirring just before the expiration of the time. Then weigh the liquid and calculate the percentage of separable liquid. At the end of the 5 minutes a considerable amount of liquid is still left with the tomatoes, but the great bulk of easily-separable liquid will have drained away. Five minutes seems to be about the right length of time to allow for drainage, as the object is not to get out all of the possible liquid, but that portion which is easily separable in order to determine whether water has been added and whether the tomatoes are of good quality.

Seventy-seven cans were examined in this manner; of that number 66 were the two, 6 the two and one-half and 5 the one and one-half pound cans. The average easily-separable fluid was 52 per cent, with the lowest 38 per cent and the highest 64.4 per cent. About 60 per cent came between 47 and 57 per cent of separable liquid. In the majority of cases each sample represented a different brand. but in many cases duplicate and triplicate samples were examined, and different cans of the same brand of the same pack were found to vary greatly. In one case the separable liquid varied from 44 to 69 per cent with a difference of 16 per cent, in another case from 47 to 57 per cent, while in others the variation was about 1 per cent.

In all of the cans the tomatoes were in good condition. In some cases the tomatoes had been selected and prepared with more care than in others, but in no case was there found any evidence of added water, although it could not be told positively that none had been added. As a result of this work canned tomatoes which do not contain more than 50 per cent of separable fluid are considered by the associate referee to be excellent. Of course, tomatoes will vary from year to year in the amount of juice they contain and probably will vary at different seasons of the same year. A point which was not considered and which may have an influence on the separable liquid is the length of time the tomatoes have been canned.

At the end of the work the total contents of the can and the separable liquid were measured in a graduated liter cylinder and the results agreed very closely with the results obtained by weighing. It is the opinion of the associate referee that the method of measuring could be substituted for weighing with advantage because of the saving of time which would thus be accomplished. This point, however, needs further study.

It is recommended—

(1) That the associate referee for the ensuing year make determinations of the easily-separable liquid in canned tomatoes, corn, and butter beans, paying especial attention to the size and kind of sieve and to the time allowed for drainage, and in the case of tomatoes to the effect of the age of the canned product on the amount of easily separable fluid.

REPORT ON COCOA AND COCOA PRODUCTS.

By H. C. Lythgoe, *Associate Referee.*

MILK SOLIDS IN MILK CHOCOLATE.

The present methods of the association for the determination of milk fat and lactose are satisfactory. The method of Baier and Neumann (*Zts. Nahr. Genussm.*, 1909, **18:** 17) for the determination of casein was

studied last year and proposed as a provisional method. Several samples of commercial milk chocolate were obtained and analyses made by myself and my assistants, the results of which are as follows:

Analyses of milk chocolate.

SAMPLE NO.	MOISTURE	ASH	NITROGEN	CASEIN	TOTAL MILK PROTEINS	FAT	REICHERT-MEISSL NUMBER	MILK FAT	SUCROSE	LACTOSE	MILK PROTEINS × 1.454	MILK PROTEINS DIVIDED BY MILK FAT	MILK SOLIDS
1..........	1.48	1.90	1.34	3.14	3.92	33.09	4.51	5.64	38.63	4.84	5.70	0.69	15.26
2..........	1.32	2.30	1.49	3.90	4.87	32.04	5.01	6.18	36.08	6.50	7.04	0.79	18.57
3	2.06	2.26	1.92	3.69	4.62	24.12	5.17	5.82	44.89	6.22	6.72	0.79	17.63
4..........	0.70	1.97	1.26	2 46	3.08	31.18	2.79	3.26	43.64	4.35	4.48	0.94	11.37
5..........	1.30	1.84	1.20	3.29	4.11	33.93	4.29	5.47	41.02	6.58	5.97	0.75	17.20
6..........	1.22	2 00	1.36	4.00	5.00	30.16	5.83	6.84	42.19	8.47	7.27	0.73	21.62

Composition of milk used.

SAMPLE NO.	SOLIDS	FAT	PROTEINS	ASH	SOLIDS NOT FAT	LACTOSE	PROTEIN FAT RATIO
1.	15.03	5.59	3.89	0.75	9.44	4.80	0.69
2	13.70	4.56	3.59	0.75	9.14	4.80	0.79
3	13.59	4.48	3.56	0.75	9.11	4.80	0.79
4...........	12.55	3.60	3.40	0.75	8.95	4.80	0.94
5	12.54	3.99	3.00	0.75	8.55	4.80	0.75
6	12.26	3.88	2.83	0.75	8.38	4.80	0.73

CALCULATION OF THE COMPOSITION OF THE MILK USED.

Milk proteins were calculated by multiplying the per cent of casein by 1.25. About 80 per cent of the total milk proteins is casein, the balance albumin. Milk sugar and ash are the least variable of all the constituents of milk. The sugar will vary in herd milk from 4.3 to 5.3 per cent, and from 4 to 5.8 per cent in milk from individual cows. The average milk sugar of 437 samples of milk of known purity examined during the past six years by the Massachusetts State Board of Health is 4.78 per cent, and of 47 samples of herd milk is 4.83 per cent. For the calculation of the composition of the original milk, 4.8 per cent was assumed to be the sugar content and 0.75 per cent the ash content and the computation was made by proportion. Thus in Sample 2, the milk sugar found was 6.50 per cent, the milk proteins 4.87

$$6.50 : 4.80 = 4.87 : x$$

$x = 3.59$, the per cent of proteins in the milk.

The sum of the fat, proteins, lactose, and ash gives the total solids and by proportion the total milk solids in the chocolate was obtained. For example, in Sample 2, the milk solids of the milk used was found to be

13.70 per cent, the lactose (assumed) 4.80 per cent, the lactose in the chocolate was 6.50 per cent.

$$4.80 : 6.50 = 13.70 : x$$
$$x = 18.59 \text{ per cent of milk solids in chocolate.}$$

DISCUSSION OF RESULTS.

The best comparison of the figures are those comparing the calculated values with actual milk analyses, which are shown in the following table:

Analyses of milk.

	SOLIDS	FAT	PROTEINS	ASH	LACTOSE	PROTEIN FAT RATIO
Sample	15.03	5.59	3.89	0.75	4.80	0.69
Average of 10 samples of milk	15.00	5.62	3.75	0.76	4.87	0.67
Sample 2	13.70	4.56	3.59	0.75	4.80	0.79
Average of 10 samples	13.70	4.59	3.40	0.75	4.77	0.74
Sample 3	13.59	4.48	3.56	0.75	4.80	0.79
Average of 10 samples	13.60	4.67	3.40	0.75	4.78	0.73
Sample 4	12.55	3.60	3.40	0.75	4.80	0.94
Average of 10 samples	12.50	3.99	2.84	0.73	4.94	0.71
Sample 5	12.54	3.99	3.00	0.75	4.80	0.75
Average of 10 samples	12.50	3.99	2.84	0.75	4.94	0.71
Sample 6	12.26	3.88	2.83	0.75	4.80	0.73
Average of 10 samples	12.30	3.89	2.81	0.72	4.88	0.70

According to the above comparisons all the calculated values are normal for milk of the same solids except 4, and the conditions found here may be due to the use of some skimmed milk. Assuming the average milk protein to be 3.30 per cent and the average sugar to be 4.80, the percentage of milk proteins multiplied by 1.454 would give the percentage of lactose. This ratio, however, varies with the composition of the milk used. The value with milk of 11.5 per cent of solids would be 1.8 and with milk of 14 per cent of solids would be 1.42. Therefore, not very reliable comparisons between the found and calculated lactose can be expected unless the milk used contained about 13 per cent of solids.

The protein-fat ratios show that the methods for both casein and milk fat give results which are to be expected in products made from milk and are, therefore, reliable methods. The methods for casein and milk fat were tried upon a sample of malted milk with the following results: Fat 7.09 per cent, Reichert-Meissl number 27.6, casein 6.65 per cent. The method for casein applied to a proprietary food containing casein gave the following results: Total proteins (N $\times$ 6.38), 79.66 per cent; casein 79.68 per cent.

It is recommended that the methods for the determination of casein and milk fat as proposed last year be adopted as provisional.

REPORT ON TEA AND COFFEE.

By J. M. Bartlett, *Associate Referee.*

As no report on methods of analyses for tea and coffee was given in 1912 the associate referee for 1913 was referred to the report of 1911, when a study of methods for the determination of caffein was made with recommendations that these methods be given further study. Therefore, the work has been confined to that subject. The Gorter and the modified Stahlschmidt methods, together with one suggested by H. C. Fuller of the Institute of Industrial Research, were selected as the most promising for the work. Five chemists signified a desire to take part in the work and in May a sample of tea and one of coffee were sent them. These samples were prepared by grinding and mixing thoroughly several pounds of material which had been purchased on the market. The following instructions were sent with each set of samples:

INSTRUCTIONS TO COLLABORATORS.

Determine caffein or thein in each of the samples by the following methods:

FULLER METHOD FOR TEA AND COFFEE.

Weigh carefully 10 grams of No. 60 powder into a 500 cc. Erlenmeyer, add 100 cc. of water, 10 cc. of 10 per cent hydrochloric acid, and heat to boiling with a reflux condenser for 2 hours. Cool, decant liquid through a filter, treat solid material with 3 portions, 50 cc. each, of boiling water, filtering through same paper as just used and wash material on filter with 50 cc. of boiling water. Concentrate to 150 cc. by evaporating over steam or water bath. Transfer filtrate to a 500 cc. separator, Squibb type, add 5 cc. of stronger ammonium hydroxid, shake out with 50 cc. portions of chloroform five times. After the first shaking out let the separator rest until the separation is as complete as it will be; then run chloroform into another 500 cc. separator; add the second portion of chloroform and shake again, after standing until no further separation occurs, run the solvent and the adhering emulsion, if any, into the second separator, but do not run any of the nonemulsified liquid.

Repeat three times, running chloroform and any emulsion into the second separator. Then discard the liquid in the first separator and give the second separator containing the chloroform and emulsion a violent shaking; let stand and then run chloroform into a 250 cc. Erlenmeyer flask. If there is an emulsion remaining in the separator, add 1 to 5 cc. of 94 per cent alcohol and shake. When the chloroform has separated, add it to that in the 250 cc. flask. Add about 25 cc. of chloroform to the aqueous alcoholic layer in the separator and agitate; after separation run the chloroform into the 250 cc. flask and then evaporate off the chloroform on the steam bath using a moderate blast of air and removing from bath as last portions evaporate to avoid spattering. When the residue of crude caffein is dry add 10 cc. of dilute hydrochloric acid (10 per cent) and 50 cc. of water and warm until caffein is dissolved. Cool and precipitate with 50 cc. of iodin solution (10 grams of iodin, 20 grams of potassium oxid, 100 cc. of water), stopper flask with cork and let stand overnight.

Filter through 9 cm. filter and refilter filtrate, if necessary, washing flask and precipitate twice with iodin solution, but not attempting to remove all of the precipi-

tate from the flask. Transfer filters to flask in which precipitation was made, add 0.5 gram of sodium acid sulphite, or sodium sulphite, 3 cc. of 10 per cent sulphuric acid and 15 cc. of water and warm until iodid is decomposed, more salt being added if the amount is insufficient to decolorize.

Filter into a separator (small 100 cc.), add excess of stronger ammonium hydroxid and shake out 5 times with 15 cc. portions of chloroform. Wash the combined chloroform extracts with water which is discarded, and then concentrate to 10 to 15 cc.; add dry animal charcoal, shake and allow to stand one hour with occasional shaking; filter through a small filter into a tared dish, wash flask and filter 3 or 4 times with 5 cc. portions of chloroform. Evaporate chloroform, dry residue in a desiccator and weigh.

GORTER METHOD FOR COFFEE.

Moisten 11 grams of finely-powdered coffee with 3 cc. of water, allow to stand for half an hour, and extract for 3 hours in a Soxhlet extractor with chloroform. Evaporate the extract, treat residue of fat and caffein with hot water, filter through a cotton plug and moistened filter paper, and wash with hot water. Make up the filtrate and washings to 55 cc., pipette off 50 cc. and extract four times with chloroform. Evaporate this chloroform extract in a tared flask and dry the caffein at 100°C. and weigh. Transfer residue to Kjeldahl flask with a small amount of hot water and determine nitrogen by Kjeldahl or Gunning method. $N \times 3.464 =$ caffein.

MODIFICATION OF THE STAHLSCHMIDT METHOD FOR TEA.

Boil 6 grams of finely-powdered tea in a flask with several successive portions of water for 10 minutes each, and make up the combined aqueous extracts thus obtained to about 550 cc. with water. Add 4 grams of powdered lead acetate to the decoction, boil for 10 minutes, using a reflux condenser, then add water so that the solution will finally be exactly 600 cc. Then pour the solution upon a dry filter and evaporate 500 cc. of the filtrate, corresponding to 5 grams of the tea, to about 50 cc. and add enough sodium phosphate to precipitate the remaining lead. Filter the solution, and thoroughly wash the precipitate, evaporate the filtrate and washings to about 40 cc. Finally, extract the solution thus concentrated with chloroform in a separatory funnel at least four times and evaporate the chloroform extract to dryness, leaving the caffein, which is dried to constant weight at 75°C. and weighed.

The associate referee will be very glad if other methods are being used in the work of the analysts to determine caffein, to have results by such methods reported, and the methods given in detail.

RESULTS OF COÖPERATIVE WORK.

COMMENTS OF ANALYSTS.

H. C. Fuller: I would suggest that in running the Gorter method, when the aqueous liquid is to be shaken out with chloroform it should be made ammoniacal in order to hold back certain coloring matter and facilitate in the extraction of caffein. In the Stahlschmidt method for tea, it seems to me that the directions are not sufficiently explicit when it states that the solution should be made up to exactly 600 cc. According to the directions given, this could be done either in the hot or cold solution, and if it is done hot and it is attempted to filter 500 cc., the hot solution will have a chance to evaporate somewhat, and, of course, it is cooling all the time it

is filtering—hence, becoming more concentrated, so that when you finally determine your caffein you will be working with a proportion which represents really more than 5 grams of tea. I think this is one reason why we obtained higher results by this method than by my own.

Results of analysis of coffee and tea.

ANALYST	CAFFEIN IN COFFEE			CAFFEIN OR THEIN IN TEA	
	Gorter method		Fuller method	Modified Stahlschmidt method	Fuller method
	Gravimetric	Nitrogen × 3.464			
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
H. C. Fuller, Institute of Industrial Research, Washington, D. C.	1.270	[1]0.850	1.170	3.140	2.850
F. F. Exner, Bureau of Chemistry, Washington, D. C.	1.335 1.335 1.384 1.344	1.185 1.123 1.282 1.246 1.220 1.158	1.246 1.242	3.306 3.170 3.134 3.178 N × 3.4643 3.073 3.054 2.995 3.054	2.704 2.482
H. B. St. John, Bureau of Chemistry, Washington, D. C.	[2]1.777	1.264	1.195	2.916	2.720
E. E. Sawyer, Agricultural Experiment Station, Orono, Me.	1.230 1.220	1.205 1.230	1.204 1.213	2.782 2.800	2.783 2.819
Average	1.287	1.211	1.211	3.055	2.735

[1] Omitted from average.
[2] Purified by shaking out with sodium carbonate solution.

B. H. St. John: It seems to me that the Gorter method could be successfully modified as follows: After shaking out the aqueous solution with chloroform, run the chloroform into a second separator and shake with a strong solution of sodium carbonate. The sodium carbonate solution will remove most of the coloring matter. Then pass the chloroform to a third separator and wash with water. Treat the remaining chloroform shakeouts from the aqueous solution in the same manner, passing them successively through the sodium carbonate and wash water. Unite the washed chloroform extracts, evaporate, dry and weigh, and put through the method of purification given in the Fuller method. I have given the results of one sample run in this manner. The results obtained by the modification suggested, represents only a limited amount of work. From the analyses of the samples in question, however, together with the results obtained upon a number of samples of medicated soft drinks, the modification suggests itself to me as being worth further work to determine whether or not it will be of value.

F. F. Exner: The Fuller method is laborious, time consuming, and by no means accurate. With tea the initial extraction with water is incomplete. This was proved by using the tea residue from two extractions in one portion, pouring more water over it, letting this stand on the steam bath for 2 hours, filtering and treating the filtrate as above for caffein; 0.028 gram of caffein was obtained. This would be 0.014 gram for each portion, which probably accounts for the low results obtained

with the tea. The first extraction with chloroform is difficult because of persistent emulsions especially with the tea. The caffein obtained from the tea is fairly white and pure, both by one sublimation, or by the iodin precipitation, so that the use of charcoal is not necessary. With coffee the first extraction with water seemed to be complete. Further extraction of the residue gave only a negligible amount of the additional caffein. The emulsion of the first chloroform extraction is not so persistent as is the case with the tea, but the caffein was still colored yellowish when purified by two sublimations or by the iodin purification. The two methods of purification are about equally efficient, but the sublimation is much shorter and simpler. The attempt to purify the caffein further by means of bone black proved unsuccessful. Though some of the color was removed, the caffein was not entirely white after this operation. It is very difficult to recover all the caffein upon filtering; although the charcoal and filter were thoroughly washed with chloroform, the 0.1246 gram of caffein from Experiment 2 with coffee, yielded only 0.1020 gram after treating with charcoal.

In the Gorter method for coffee the initial extraction is convenient and complete. I used a large extractor with a large paper thimble $1\frac{1}{4}$ inches in diameter. I found it much better to remove the fat from the crude extract with petroleum ether, before dissolving the caffein in hot water. This was done as follows: Pour 5 cc. of petroleum ether on the extract, dissolve the fat and decant the liquid through a small cotton plug in the stem of a small funnel. Repeat three times with 3 cc. portions of fresh petroleum ether; catch the filtrate in a small beaker and evaporate the ether off on the steam bath. Exhaust the caffein residue with boiling water according to the instructions, and filter through the same funnel and cotton plug, the filtrate being received in the separating funnel. Finally pour 5 cc. of hot water on the oil in the small beaker, heat the mixture and pour the whole onto the same filter at once. In this way all the water extract will run through the filter before it becomes clogged with the oil. A clean filtrate is obtained in which the subsequent extraction with chloroform is very rapid.

Caffein is nearly insoluble in petroleum ether, but any traces that may have dissolved with the fat will be recovered by the subsequent treatment of the fat with water. There was a question in my mind as to whether the large amount of impurities in the residue from the second chloroform extract might not contain nitrogen and so yield high results by the Kjeldahl method. I thought, therefore, to try a new form of sublimator which the writer has used with satisfaction on benzoic acid. It was thought that purification might be brought about and the caffein weighed directly. But the sublimate from the first sublimation was always of a pale sulphur yellow color, and after the second sublimation, a pale cream color. The second sublimate seems fully as pure as the results obtained by the Fuller method in the iodin treatment, but compared with the nitrogen estimation, the results are still high.

Experiments 8 and 9 (see table following) show that the nitrogen determination is probably reliable, even when the crude, unpurified caffein is treated by the Kjeldahl method, so the attempted purification by sublimation is not necessary. Indeed even though the results from the second sublimation are still somewhat high, there has been sustained a slight loss of caffein, for when the second sublimate is treated by the Kjeldahl method, the results are somewhat lower than in Experiments 8 and 9. Experiments 12 and 13 were for the purpose of checking the nitrogen method on pure material, and the results are entirely favorable.

The modified Stahlschmidt method for tea proved on the whole quite satisfactory. I made the first extractions with 150 cc. of water and repeated the operation five

times with 100 cc. of water. The lead acetate was added as directed before the last extraction was made. This last portion was used for the final filling to the mark. In this way the extraction was practically complete. To test this, the residues from the four experiments were combined and heated for several hours with water. The liquid was treated separately for caffein and only 4 mg. were obtained. This would be 1 mg. for each portion. The caffein as first weighed had considerable color, and the result is doubtless high. One sublimation gave a product of a good white color, though the solution of the sublimate in chloroform still had a slight yellow tint. Instead of the sublimation the nitrogen determination may also be used, and I believe we are justified in placing confidence in the result. The sublimation weight will doubtless always be slightly higher, but either method of purification may be considered satisfactory here.

Results of sublimation of caffein in coffee.

METHOD AND EXPERIMENT	COFFEE USED	CRUDE CAFFEIN	CAFFEIN IN FIRST SUBLIMATION		CAFFEIN IN SECOND SUBLIMATION		CAFFEIN PURIFIED BY IODIN PRECIPITATION		NITROGEN	N × 3.4643 = CAFFEIN	
FULLER METHOD:	*grams*	*gram*	*gram*	*per cent*	*gram*	*per cent*	*gram*	*per cent*	*gram*	*gram*	*per cent*
1.	10	......	0.1316	1.316	0.1288	1.288	......	.....	....	....	......
2.	10	......	......	...	....	....	0.1246	1.246	......	......	......
3.	10	......	......	.....	.....	.....	0.1246	1.246	....	....	......
GORTER METHOD:											
1.	11	0.1931	0.1578	1.438	0.1468	1.335	......	.....	....	....	......
[1] 2.	11	0.2067	0.1587	1.443	Loss	.	......	.....	.....	......	......
[1] 3.	11	0.1540	0.1361	1.237	......	.....	......	.....	....	....	......
[1] 4.	11	Loss	......	......	......	....	......	.....	......	......	......
5.	11	0.1936	0.1539	1.399	0.1468	1.335	......	.....	Loss	....	......
[1] 6.	11	0.1852	0.1478	1.344	......	.....	......	.....	0.037614	0.13031	1.185
[1] 7.	11	0.1614	0.1366	1.242	......	.....	......	.....	0.035649	0.12350	1.123
8.	11	......	......	.....	......	.....	......	.....	0.040702	0.14100	1.282
9.	11	......	......	.....	......	.....	......	.....	0.039580	0.13704	1.246
10.	11	0.2330	0.1622	1.475	0.1522	1.384	......	.....	0.038740	0.13420	1.220
11.	11	0.1994	0.1520	1.382	0.1478	1.344	......	.....	0.037333	0.12733	1.158
12.	..	0.3060	c. p. anhydrous caffein taken				......	.....	0.087859	0.30437	99.460
13.	..	0.2794	do				......	.....	0.071000	0 27714	99.190

[1] Loss in extraction; results not comparable, except to show relation between sublimation and nitrogen results. Experiments 1, 5, 8, 9, 10, 11, 12 and 13, should be given chief weight. No. 2 is all right as far as it goes.

Results of sublimation of caffein in tea.

Fuller method.

EXPERIMENT NO.	TEA USED	CAFFEIN IN FIRST SUBLIMATION		CAFFEIN PURIFIED BY IODIN PRECIPITATION	
	grams	*gram*	*per cent*	*gram*	*per cent*
1.	10	0.2542	2.542	......	.....
2.	10	......	.....	0.2704	2.704
3.	10	......	.....	0.2482	2.482
4.	10	0.2724	2.724	......	.....

Modified Stahlschmidt method.

EXPERIMENT NO.	TEA USED	CAFFEIN FROM 5 GRAMS OF WEIGHED EXTRACT		CAFFEIN FROM 3 SUBLIMED		NITROGEN FROM 5	N × 3.4643 = CAFFEIN	
	grams	*gram*	*per cent*	*gram*	*per cent*	*gram*	*gram*	*per cent*
1.......	6	0.1802	3.604	0.1653	3.306	0.044351	0.15365	3.073
2.......	6	0.1614	3.228	0.1585	3.170	0.044070	0.15267	3.054
3.......	6	0.1594	3.188	0.1567	3.134	0.043228	0.14976	2.995
4.......	6	0.1614	2.228	0.1589	3.178	0.044070	0.15267	3.054

NOTE BY ASSOCIATE REFEREE.

The results on the whole by all three methods are quite satisfactory with the coffee, but it is evident that the Fuller method gave rather low results on tea. It is evident that the Gorter method yields the caffein in a somewhat impure condition and it is necessary to determine the nitrogen in the residue in most instances to arrive at a correct result. The Fuller method, on the other hand, yields the caffein in a fairly pure condition and in the case of coffee the results obtained agree very closely with those obtained by the Gorter method when calculated from the nitrogen determined. If some modifications can be introduced into the Fuller method to facilitate the extractions and filtrations in the first part of the method, which are now very tedious and somewhat incomplete, particularly in the case of tea, it could possibly be made an accurate and desirable method for both tea and coffee.

RECOMMENDATIONS.

It is recommended—

(1) That the Fuller method for determination of caffein in tea and coffee be further studied with a view to improving the method of extraction and filtration.

(2) That the Gorter method be further studied with a view to purifying the caffein with sodium carbonate solution for direct weighing.

(3) That the modified Stahlschmidt method be given another trial for the determination of thein in tea.

THE SUBLIMATOR AND ITS USE.

By F. F. Exner.

The substance to be sublimed is placed in the bottom of the sublimation flask. It can be weighed in the flask, for this is composed of an ordinary beaker flask of light glass and 10 ounce capacity. The glass coil is fitted to slip easily through the perforations in the cork, yet the apparatus should not leak. The bottom of the cork which goes inside the flask is covered with a disk of tin foil. Through a third perforation in the cork is slipped a glass tube about 10 cm. long, its lower end being flush with

the bottom of the cork. The apparatus is supported on a wire gauze with asbestos, on a stand above a Bunsen burner. The ends of the glass coil are connected with rubber tubes to the tap so that a slow current of water will pass through the coil. The bottom of the flask is gently heated with a flame about 1 inch high under the asbestos. The caffein soon begins to sublime and condense on the cooled coil. When most of the substance has been driven from the bottom, a second flame, slightly yellow and rather large, but not too intense, is rapidly played around the sides of the flask until all has been completely volatilized and condensed on the coil. If some of the sublimate seems loose, the apparatus is shaken a little, and if anything falls off the coil it is again sublimed to the coil. When complete the apparatus is allowed to cool, the rubber tubes are disconnected, the apparatus carefully lifted from the stand, then the coil with the cork are lifted gently from the flask and placed in the

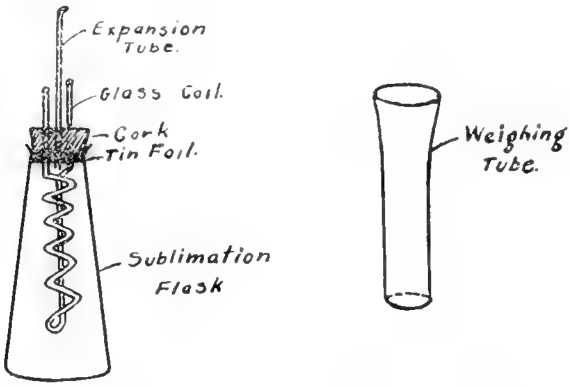

FIG. 2. *a.*–SUBLIMATOR. *b.*–WEIGHING TUBE.

weighing tube. This is then supported on the stand and the stem of a funnel is attached to one coil and a double bend glass tube to the other. First alcohol, then ether, is run through the coil, and finally a current of air to dry it. The coil is then slipped from the cork, the tin foil being loosened and left with the coil. This is placed in a desiccator and weighed. Previous to the sublimation the apparatus was weighed in the same way. The difference gives the sublimate.

The expansion tube. This has a small rather loose plug of cotton in the upper end, and is weighed separately before and after the sublimation. There is usually from 0.6 to 1.5 mg. of the sublimate in this tube.

For benzoic acid which sublimes nicely from 120° to 140°C., the writer uses a glycerol bath. The caffein can be sublimed also in a glycerol bath, but the fumes are annoying. A convenient air bath could readily be devised, but the above procedure does so well that it is hardly worth while to use these accessories.

REPORT ON PRESERVATIVES.

By A. F. Seeker, *Associate Referee.*

The work this year has been confined entirely to the detection and determination of formic acid. An examination of the literature indicates that small amounts of formic acid may exist naturally in certain products or may be found in small amounts during the process of distillation required to separate it in the pure condition necessary for a qualitative test. It has been found[1] that formic acid is formed during the fermentation of sugars by yeast and is also decomposed during the same process so that little, if any, finally remains. The question of its presence in honey is still open, though the work of Fincke,[2] Farnsteiner,[3] and Heiduschka and Kaufmann[4] shows that the amount present is in any event less than 0.02 per cent, many samples showing none at all. It is also said to be produced by the slow oxidation of some terpenes in the presence of moisture[5] which would lead to traces being found in some products flavored with essential oils. Further it has been shown[6] that small amounts of formic acid are formed when carbohydrates are distilled in acid solution, Kreis expressing the opinion that qualitative tests are for this reason of no value and that quantitative results alone will indicate the presence or absence of added formic acid. In view of these statements contained in the literature, the plan adopted for this year's work was as follows:

(1) To select what appeared to be the most satisfactory method for determining formic acid and to test its accuracy upon some simple mixtures.

(2) To examine as many food products as possible with a view of ascertaining how much formic acid (or what appears to be formic acid) exists in them naturally or is produced in them by the operations required for its determination.

(3) To submit to collaborators for analysis samples of food products containing known amounts of added formic acid together with a detailed description of the method for its determination.

A study of the quantitative methods that have been proposed, a comprehensive bibliography of which may be found in Fincke's paper on "The Detection and Determination of Formic Acid"[7] would indicate that the reduction of mercuric chlorid and weighing of the resulting mercurous salt would yield the best results for practical purposes. The

[1] Franzen, *Chem. Ztg.*, 1911, **35**: 1097; Franzen and Steppuhn, *Zts. Physiol. Chem.* 1912, **77**: 129.

[2] *Zts. Nahr. Genussm.*, 1912, **23**: 255.

[3] Ibid., 1908, **15**: 598.

[4] Ibid,, 1911, **21**: 375.

[5] Kingzett and Woodcock, *Chem. News*, 1912, **105**: 26; *J. Soc. Chem. Ind.*, 1910, **29**: 791.

[6] Fincke, *Zts. Nahr. Genussm.*, 1911, **21**: 13; Kreis, *Mitt. Lebensm. Hyg.*, 1912, **3**: 205; 266.

[7] *Biochem. Zts.*, 1913, **51**: 253.

method of Wegner[1] depending upon the formation of carbon monoxid by treating formates with concentrated sulphuric acid[2] has also been strongly recommended and may prove of value for confirmatory purposes, but appears to be too elaborate for general use.

The procedure selected was that devised by Heinrich Fincke[3] which consists in distilling the material, acidified with tartaric acid, in a current of steam, passing the vapors through a boiling suspension of calcium carbonate in water, the vapors being then condensed and collected in order to measure the amount of vapor that has been passed through the sample. The calcium carbonate mixture is filtered and formic acid determined in the filtrate by reduction of mercuric chlorid. The points to be particularly observed in this procedure are:

(1) That the volume of the sample shall not exceed 100 cc. and that it be kept at that volume throughout the distillation.

(2) That not less than 1,000 cc. of distillate be collected.

(3) That the substance shall contain no free mineral acid.

(4) That sulphurous, sorbic, glyoxylic, levulinic, and fumaric acids are absent.

Regarding the first two points Fincke found that with 100 cc. of substance and 1 liter of distillate, 90 to 95 per cent of the formic acid is recovered. By increasing the amount of substance or by decreasing the amount of distillate the percentage of recovery rapidly diminishes.

These statements have been confirmed by the associate referee, as the following results show:

Substance	*Amount of distillate. cc.*	*Formic acid recovered. per cent.*
0.0992 gram of formic acid, 100 cc. of water	200	52
0.0992 gram of formic acid, 100 cc. of water	500	85
0.0992 gram of formic acid, 100 cc. of water	1000	96
0.0992 gram of formic acid, 50 cc. of water	1000	98
0.0992 gram of formic acid, 150 cc. of water	1000	85

It has been found as pointed out by Fincke that formic acid is produced upon distilling solutions of carbohydrates containing free mineral acid, and methods based upon this procedure, several of which have been proposed, are certain to give high results.

[1] *Zts. Anal. Chem.*, 1903, **42**: 427.

[2] Ost and Klein, *Chem. Ztg.*, 1908, **32**: 815; Merl, *Zts. Nahr Genussm.*, 1908, **16**: 389; Röhrig, Ibid., 1910, **19**: 1.

[3] *Zts. Nahr. Genussm.*, 1911, **21**: 1; 1911, **22**: 88; 1912, **23**: 255; 1913, **25**: 386; and *Biochem. Zts.*, 1913, **51**: 253.

The following experiments by the referee show this to be true:

Composition of solution distilled	*Grams of formic acid found.*
50 grams of sucrose, 2 grams of tartaric acid, 100 cc. of water	0.0024
50 grams of sucrose, 2 cc. of 85 per cent phosphoric acid, 100 cc. of water	0.0102
50 grams of sucrose, 1 cc. of 85 per cent phosphoric acid, 50 cc. of water	0.0639
50 grams of sucrose, 5 cc. of 85 per cent phosphoric acid, 50 cc. of water	0.2157
A commercial chocolate fountain sirup (total solids 70 per cent, sucrose 53 per cent) in a dilution of 50 grams to 250 cc., acidified with 5 to 10 cc. of 20 per cent phosphoric acid	0.1021
Same chocolate sirup in same dilution acidified with 2 grams of tartaric acid	0.010

Concerning the nature of interfering substances and their removal, only the effect of the common preservatives, sulphurous, benzoic and salicylic acids have been studied. In his early work Fincke sometimes used a barium carbonate suspension instead of calcium carbonate for absorbing the vapors of formic acid, but in his later work for unexplained reasons, only calcium carbonate was used. It is well known that barium sulphite is comparatively insoluble in hot water and it was thought probable that by substituting barium carbonate for calcium carbonate in Fincke's procedure the interference of sulphurous acid could be eliminated. As a test of this theory a mixture of 100 cc. of water, 2 grams of barium carbonate, and 5 cc. of a saturated solution of sulphur dioxid in water were mixed in the cold and filtered. The filtrate was reduced in the regular way and yielded the equivalent of 0.0037 gram of formic acid as mercurous chlorid. A mixture of the same composition as the above was then prepared and boiled before filtering, the last operation being conducted while hot. The reduced mercury salt amounted to the equivalent of 0.0010 gram of formic acid.

The next experiments were conducted in the manner of the regular Fincke determinations using a suspension of barium carbonate instead of calcium carbonate.

Composition of solution	*Reduction equivalent to grams of formic acid.*
75 cc. of lime juice, 25 cc. of water	0.0026
75 cc. of lime juice, 25 cc. of water, 100 mg. of sulphur dioxid	0.0032
75 cc. of lime juice, 25 cc. of water, 100 mg. of sulphur dioxid	0.0041
100 cc. of cherry juice, 2 grams of tartaric acid, 0.2 gram salicylic acid.	0.0026
50 grams of strawberry sirup, 0.05 gram of benzoic acid, 2 grams of tartaric acid, 50 cc. of water	0.0015

With these preliminary tests completed the method as follows was adopted for trial:

FINCKE METHOD FOR FORMIC ACID.

APPARATUS.

A device for generating steam.

A 300 cc. round bottom flask (hereafter designated A).

A 500 cc. round bottom flask (hereafter designated B).

A condenser and a receiver in which the distillate may be measured.

When in operation the steam passes through the liquid in flask *A* and then into the next flask by way of a spray trap and connecting tube the end of which reaches almost to the bottom of flask *B* and is furnished with a special tip consisting of a bulb containing a number of small holes for the purpose of breaking the vapor into small bubbles. From the second flask the vapor passes into the condenser and from thence the distillate passes into the receiver which is graduated to show a content of 1 liter.

PROCEDURE.

For thin liquids like fruit juices use 50 cc.

For heavy liquids and semi-solids like sirups and jams use 50 grams diluted with 50 cc. of water.

Place the sample in flask *A*, add 1 gram of tartaric acid (samples like lime juice which are naturally very acid need not be acidified), heat to boiling and steam distill, passing the vapor through a boiling suspension of 2 grams of barium carbonate in 100 cc. of water contained in flask *B*. If the sample contains much acetic acid more barium carbonate must be used in order that an excess of 1 gram remains at the end of the operation. The vapor issuing from flask *B* is condensed and measured. Continue the distillation until 1 liter of distillate is collected, the volume of liquid in flasks *A* and *B* being maintained as nearly constant as possible by heating with small Bunsen flames. After 1 liter of distillate has been collected disconnect the apparatus and filter the contents of flask *B* while hot, washing the barium carbonate that remains on the paper with a little hot water. The filtrate and washings should now measure between 100 and 150 cc. If not, it should be boiled down to that volume. Add 10 cc. of sodium acetate solution (50 grams of dry salt per 100 cc), 2 cc. of 10 per cent hydrochloric acid, and 25 cc. of mercuric chlorid reagent (100 grams of mercuric chlorid, 150 grams of sodium chlorid dissolved in sufficient water to make 1 liter). Mix thoroughly and immerse the container in a boiling water bath or steam bath for 2 hours. Filter on a tared Gooch, wash thoroughly with cold water and finally with a little alcohol. Dry in a boiling water oven for half an hour, cool and weigh. The weight of mercurous chlorid obtained multiplied by the factor 0.0975 gives the weight of formic acid present. If the weight of mercurous chlorid exceeds 1.5 grams the determination must be repeated using more mercuric chlorid reagent or a smaller amount of sample.

A blank test should be conducted with each new lot of reagents employed in the reduction, using 150 cc. of water, 1 cc. of 10 per cent barium chlorid solution, 2 cc. of 10 per cent hydrochloric acid, 10 cc. of 50 per cent sodium acetate solution, and 25 cc. of mercuric chlorid reagent. The weight of mercurous chlorid obtained in this blank test should be deducted from that obtained in the regular determination.

RESULTS.

A standard solution of formic acid to be used in testing the method was prepared and standardized both by titration and by reduction.

By titration. Grams per 100 cc.		*By reduction. Grams per cc.*
0.00993		0.00990
0.00994		0.00995
		0.00991
		0.00990
	Average,	0.00992

In the reduction method a blank reduction test was conducted upon the reagents and deducted from the individual determinations.

The method applied to 50 cc. of aqueous solution containing 0.0992 gram yielded 0.0979 gram of formic acid or 98.7 per cent recovery.

Further tests of the method gave the following results:

AMOUNT OF MATERIAL TAKEN	FORMIC ACID ADDED	FORMIC ACID RECOVERED	
	gram	*gram*	*per cent*
50 cc. of lime juice, 20 cc. of water	0	0.0018	....
50 cc. of lime juice, 20 cc. of standard formic acid	0.1984	0.1935	96.6
50 cc. of lime juice, 2 cc. of standard formic acid	0.0198	0.0201	101.0
42 cc. of lime juice, 7.6 cc. of standard formic acid	0.0754	0.0740	98.2
50 grams of strawberry sirup, 10 cc. of standard formic acid, 40 cc. of water	0.0992	0.0946	95.4

The following determinations were made upon a variety of products in the course of routine inspection and represent the usual blank tests by this method when added formic acid is absent. The blank test on reagents has been deducted in each case.

Determination of formic acid from inspection samples.

DESCRIPTION OF SAMPLE	FORMIC ACID FOUND IN GRAMS PER 100 CC. OR IN PER CENT BY WEIGHT
N. Y. 37530 Honey-Cuban (bulk)	0 0091
N. Y. 37023 Honey-Cuban (bulk)	0.0041
N. Y. 36713 Honey-Cuban (bulk)	0.0029
N. Y. 37025 Honey-Cuban (bulk)	0.0130
Cherry juice pressed in laboratory	0.0032
Strawberry sirup (sucrose 50 per cent) from juice pressed in laboratory	0.0009
N. Y. 37814 "Forest Pearl" summer drink sirup (in bottles)	0.0018
N. Y. 37761 Lime juice (bulk)	0.0026
N. Y. 38701 Lime juice (in bottles)	0.0019
N. Y. 39910 Lime juice fortified (in bottles)	0.0014
I. S. 23413 Blackberry jam	0.0081
I. S. 9784 Crab apple jelly	0.0051
I. S. 9786 Grape jelly	0.0083
N. Y. 40010 Raspberry juice (bulk)	0.0099
N. Y. 39038 Blackberry juice (bulk)	0.0034
N. Y. 39037 Cherry juice (bulk)	0.0043
N. Y. 39174 Prune juice (bulk)	0.0067
N. Y. 39767 Raspberry sirup (in bottles)	0.0040

During the year one sample was met with containing added formic acid, N. Y. 37809, a cherry sirup imported from Denmark in bottles, analysis

showing 0.148 per cent. Another N. Y. 38558, a raspberry shrub, contained 0.043 per cent of formic acid which probably entered the compound through the use of commercial acetic acid in its preparation.

It was found upon examining a coffee extract, I. S. 8885 E (solids 17.49 per cent) that there was a notable amount (0.063 per cent) of what appeared to be formic acid present. Upon further investigation it developed that coffee extract prepared in the laboratory from pure materials also contained formic acid, a solid extract made in this way having 0.627 per cent and a liquid extract (100 cc. representing 100 grams of original coffee) 0.061 per cent. Qualitative tests gave strong reactions for formic acid, but whether the entire reduction is due to this substance will be further investigated. The referee has reason to believe from some uncompleted work that a similar reduction may be obtained from some roasted cocoa and roasted malt preparations, but this will be more fully reported later. That the partial caramelization of sugar will cause the formation of this reducing substance seems indicated by the results of a formic acid determination in which, through faulty regulation, the substance (grape jelly) was allowed to boil down too low during the distillation, the amount of formic acid found being 0.028 per cent, whereas in a determination properly conducted the result was 0.008 per cent.

With respect to qualitative tests that of Fenton and Sisson[1] as employed by Fincke[2] has been found exceedingly delicate, 0.5 mg. being detected without difficulty. The procedure is as follows:

Introduce 10 cc. of the neutral or slightly acid liquid into a test tube, add 0.5 gram of magnesium ribbon in the form of a compact bundle, place a glass rod in the test tube upon the magnesium bundle in such a manner as to keep the magnesium at the bottom of the tube. Cool in a bath of ice water and add 6 cc. of 25 per cent hydrochloric acid a few drops at a time during an interval of about 30 minutes. When effervescence ceases test portions of the filtered liquid for formaldehyde by Leach's test. As applied to sirups and fruit juices the filtrate from the barium carbonate suspension as obtained in the quantitative determination, can be boiled down to 10 cc. for this test, or 100 to 150 cc. of an ordinary steam distillate of 50 to 100 grams of the substance are treated with barium carbonate, filtered, and the filtrate boiled down to 10 cc.

The difficulty in employing this test is its delicacy, and owing to the fact that small amounts of formic acid may be present in some natural products or are formed during the process of distillation it can not be relied upon as a means of detecting added formic acid. The associate referee has obtained positive tests with some cocoa, coffee, wine, vinegar, and with sucrose distilled in an aqueous solution made slightly acid with phosphoric acid.

[1] *Proc. Cambridge Phil. Soc.*, 1908, **14**: 385.
[2] *Biochem. Zts.*, 1913, **51**: 259.

The conversion of formates to hydrocyanic acid has been tried by means of ammonium sulphate and phosphoric anhydrid, but both it and the Grosse-Bohle reaction[1] which consists in treating 10 cc. of the solution, first with 1 to 2 cc. of 25 per cent hydrochloric acid and then with fuchsin sulphite (0.1 per cent fuchsin hydrochlorid) have not been found to give satisfactory results.

COÖPERATIVE WORK.

The collaborators this year were asked to test the accuracy of the Fincke method for the determination of formic acid. With this object in view sets of three samples were sent to each of fourteen collaborators, and seven replies were received, those cooperating being: (1) H. C. Fuller, Washington, D. C.; (2) A. L. Knisely, Portland, Ore.; (3) E. R. Lyman, Portland, Ore.; (4) F. L. Shannon, Lansing, Mich.; (5) A. W. Hanson, Kansas City, Mo.; (6) R. W. Hilts, Seattle, Wash., and (7) C. H. Robinson, Ottawa, Can. The referee wishes to express his acknowledgments to these collaborators for their assistance in this work.

The composition of the three samples sent to the collaborators was as follows:

Sample A: 302 cc. of standard formic acid solution made up to 2 liters with commercial lime juice. The lime juice employed (N. Y. 37761) was part of a shipment in bulk received at the port of New York, and previous to being used was clarified by mixing with powdered asbestos and filtering. Formic acid added, 0.1498 gram per 100 cc. A blank determination upon the original juice gave 0.0026 gram per 100 cc.

Sample B: 302 cc. of standard formic acid and 1.5 grams of sodium salicylate made up to 2 liters with cherry juice. The cherry juice was pressed in the laboratory from red cherries and clarified by mixing with powdered asbestos and filtering. Formic acid added, 0.1498 gram per 100 cc. A blank determination upon the original juice gave 0.0032 gram per 100 cc.

Sample C: 353 cc. of standard formic acid solution and 60 cc. of alcohol made up to 2,544 grams with strawberry sirup. The strawberry sirup employed was prepared by mixing 1 liter of fresh strawberry juice, pressed in the laboratory, with 1,900 grams of granulated sugar, bringing to a boil, and straining through muslin. Formic acid added, 0.1377 per cent by weight. A blank determination upon the strawberry sirup alone gave 0.0012 per cent.

[1] *Zts. Nahr. Genussm.*, 1907, **14:** 89.

RESULTS.

The results obtained by the collaborators are given in the following table:

Coöperative results on determination of formic acid.

ANALYST	SAMPLE A		SAMPLE B		SAMPLE C	
	Formic acid recovery		Formic acid recovery		Formic acid recovery	
	gram	*per cent*	*gram*	*per cent*	*gram*	*per cent*
1.....	0.1454	97.1	0.1416	94.5	0.1260	91.5
2.....	0.1496	99.9	0.1506	100.5	0.1366	99.2
3.....	0.1484	99.1	0.1468	98.0	0.1300	94.4
4.....	0.1470	98.1	0.1480	98.8	0.14	101.6
	0.1500	100.1	0.1500	100.1	0.13	94.4
5.....	0.149	99.5	0.153	102.1	......	....
	0.105	70.1	0.143	95.4	......	....
6.....	0.153	102.1	0.151	100.8	0.135	98.0
	0.153	102.1	0.150	101.1	0.136	98.7
7.....	0.142	94.8	0.1388	92.7	0.142	103.1
	0.144	96.1	0.1374	91.7	0.139	100.9

DISCUSSION.

R. W. Hilts in commenting upon the method says:

I have used this method before, or an adaptation of it, in my work, and have also used the method of Wegner as described by Röhrig and found the two methods to check very well indeed. The latter method is too elaborate for routine employment. Would it not be well to have a qualitative confirmatory test in addition to the quantitative method? I have used the following, based on Bacon's suggestion in Circular 74: Distill about 25 cc. of the sample as in the quantitative method and boil down the filtrate from the suspended carbonate to about 30 cc. (or the simpler method may be used of receiving the distillate in a flask, adding the carbonate, and boiling down and filtering). Put in a small flask. Prove the absence of formaldehyde in this solution by testing a few cubic centimeters; add 1 gram of magnesium ribbon; attach an air condenser, stand in cold water and maintain an evolution of hydrogen for 1 hour by the gradual addition of hydrochloric acid, in small quantities. Test the solution for formaldehyde by the Leach or Hehner test. For qualitative purposes only about 300 cc. of distillate need be collected. Two or 3 mg. of formic acid can be detected after reduction in this manner, in my experience. Of course, a qualitative method such as the above should be well tested out on various fruit juices before being actually proposed for adoption.

There have been no unfavorable comments upon the method from the collaborators.

The results obtained by those who have coöperated are to be regarded as particularly gratifying and prove that the Fincke method is accurate for the determination of formic acid in ordinary fruit juices and sirups. The referee feels, however, that before it can be adopted as a general method a further study should be made of interfering substances. It

appears that roasted or partially caramelized substances give high results and it is recommended that a further study of the method with reference to these as well as the interfering substances mentioned by Fincke[1] be made during the coming year. It is also recommended that the collection of data regarding the amount of volatile reducing substances occurring in natural products as determined by this method be continued, and that natural products be examined qualitatively for formic acid in order that the value of a qualitative test in detecting added formic acid may be finally ascertained.

REPORT ON WATER IN FOODS.

By W. J. McGee, *Associate Referee.*

The work for 1913 has been along the line recommended by the associate referee on this subject for 1911 and 1912, that is, the study of different dehydrating agents in drying food material in a vacuum. The investigation was extended, however, to include the study of dehydrating agents at atmospheric pressure in direct comparison with the vacuum. The highest vacuum in this experiment was about 29 inches, with an average of about 27, produced by a Schutte and Koerting water jet pump working at about a thirty-pound head. The dehydrating agents tried were: Sulphuric acid, phosphoric pentoxid, calcium carbid, metallic sodium, calcium chlorid, barium peroxid, and glycerin. The foods experimented upon were: Cheese, cocoa, and cornmeal, in the first experiment and cheese, cocoa, and raw sugar in the second experiment. The following tabulated lists show the results of the experiments.

A study of these results seems to show that sulphuric acid, phosphorus pentoxid, calcium carbid, and sodium metal are about equal in dehydrating power. Therefore, the choice for laboratory purposes may be made on the basis of other properties.

Sulphuric acid is not easily portable in a desiccator, and is perceptibly volatile when very hot dishes are placed over it, and also under other conditions which have been studied by H. C. Gore and others.

Phosphorus pentoxid is portable, but in the desiccator an impervious layer seems to form on top, which retards its action.

Calcium carbid is portable and the water absorbed converts the carbid into powder, which is easily shaken to the bottom of the receptacle. The acetylene gas formed should be given a vent with a mercury or other seal. It is possible, of course, that some classes of food would absorb acetylene gas or form additional products with it. This is not the case, however, with any of the foods so far tried.

[1] *Biochem. Zts.*, 1913, **51**: 278.

Drying in desiccators over various dehydrating agents at room temperature.

Experiment 1.

SUBSTANCE	TIME	SULPHURIC ACID		CALCIUM CARBID		METALLIC SODIUM		CALCIUM CHLORID		GLYCERIN	BARIUM PEROXID
		Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure	Atmospheric pressure	Atmospheric pressure
	days	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cheese (moisture 27.35 per cent):	1	25.50	26 30	25 51	26 32	24.61	25.56	24.03	25.85	15.81	14.93
	2	26.34	26 46	26 15	26 39	25.34	25.64	25.75	25.92	23.85	22.40
	3	26.49	26.62	26.32	26 62	25.55	25.78	26.02	25.98	24.60	23.55
	4	26.53	26.62	26 42	26 62	25.64	25.85	26.06	26.02	24.85	23.63
	5	26.44	26 46	26 44	26 55	25.66	25.89	25.95	[3]	24.90	23.97
	7	[1]26.56	[2]	26 54	[2]	25.84	[2]	26.17	.....	25.09	24.18
	9	26.70	[2]	26 64	[2]	25.90	[2]	26.29	.....	25.16	24.22
	11	26.51	26 55	26.64	27.05	25.97	24.97	26.11	.....	.....	.....
	14	.....	.....	26 51	.....	25.79	.....	26.27	.....	.....	.....
	64	.....	.....	27 28	.....	26 14	.....	26.33	.....	.....	.....
Cocos (moisture 7.41 per cent):	1	3.44	6.54	3 69	6 00	2.05	4.75	1.32	4.65	0.14	0.21
	2	5.63	6.81	5.36	6 25	3.52	5.33	3.96	4.81	1.06	0.46
	3	6.00	7.11	5 76	6 66	4.12	5.58	4.67	4.83	1.71	0.80
	4	6.22	7.11	5 94	6 75	4.75	5.76	4.86	4.90	1.95	0.91
	5	5.85	7 02	6 04	6 58	4.52	5.71	4.90	[3]	2.03	0.94
	7	[1]6.25	[2]	6 39	[2]	4.91	[2]	5.14	.....	2.27	1.07
	9	6.64	[2]	6 49	[2]	5.05	[2]	5.16	.....	2.29	1.05
	11	6.32	7 12	6.12	7.25	5.07	4.87	5.16	.....	.....	.....
	14	.....	.....	6 40	.....	4.86	.....	5.32	.....	.....	.....
	64	.....	.....	7 41	.....	5 08	.....	5.41	.....	.....	.....
Cornmeal (moisture 12.80 per cent):	1	7.54	11 15	7 51	10 86	5.42	9.65	4.26	9.20	2.05	1.40
	2	10.66	11 71	10 28	11 41	8.14	10.61	8.52	9.50	3.74	1.82
	3	11.45	12 10	11 10	11 81	9 21	11.04	9.69	9.52	5.14	2.62
	4	11.83	12 23	11 53	11 97	9.83	11.35	10.12	9.62	5.62	2.95
	5	11.58	12 29	11 67	12 03	9.98	11.50	10.24	[2]	5.79	3.07
	7	[1]12.04	[2]	12 20	[2]	10.68	[2]	10.66	.....	6.11	3.37
	9	12.57	[2]	12 50	[2]	11.03	[2]	10.87	.....	6.26	3.36
	11	12.57	13 24	12 37	13 08	11.45	10.69	10.87	.....	.....	.....
	14	.....	.....	12 57	.....	11 49	.....	11 11	.....	.....	.....
	64	.....	.....	13 92	.....	13 75	.....		.....		.....

[1] Acid renewed.
[2] Vacuum off for 45 days.
[3] Desiccator broken.

Metallic sodium forms a scale of sodium hydroxid, which, however, seems not to impair its dehydrating power. There is also danger of too much rise in temperature when a substance having a high percentage of water is placed over it. The hydrogen formed is subject to the same objections and mechanical difficulties as is acetylene gas. The objections to acetylene gas and hydrogen are not usually serious, and for ordinary laboratory work it would seem that, all things considered, calcium carbid or sodium metal are the most practical reagents.

Drying in desiccators over various dehydrating agents at room temperature.

Experiment 2.

SUBSTANCE	TIME	SULPHURIC ACID		CALCIUM CARBID		PHOSPHORUS PENTOXID		SODIUM METAL	
		Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure	Atmospheric pressure	76 mm. pressure
	days	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cheese (moisture, official method, 30.27 per cent):	1	28.38	29.08	28.32	28.85	28.46	29.35	28.48	28.88
	2	29.06	29.35	28.87	28.94	28.87	29.40	28.93	29.03
	3	29.22	29.38	29.17	29.34	29.03	29.60	29.08	29.25
	4	29.30	29 54	29.22	29.40	29.06	29.33	29.13	29.32
	5	29.28	29.41	29.22	29.48	29 13	29.64	29.13	29.13
	6	29.30	29.42	29.25	29.44	29.16	29.64	29.15	29.38
	8	29.46	29.38	29.41	29.56	29.26	29.66	29.22	29.45
	10	29.54	29.54	29.51	29.56	29.33	[1]	29.27	29.37
	16	29.57	[1]29.54	29.63	[1]29.50	29.41	29.79	29.36	29.52
	35	29.40	29.57	29.58	29.44	29.26	29.86	29.32	29.66
Cocoa (moisture 7.48 per cent):	1	4.71	6.57	4.52	6.47	5.14	6.90	5.09	5.95
	2	5.95	6.40	5.88	6.51	5.89	6.65	5.85	6.05
	3	6.30	6.89	6.25	6.98	5.73	7.15	5.97	6.38
	4	6.41	7.19	6.44	7.09	6.15	6.81	6.04	6.48
	5	6.30	6.91	6.42	7.16	6.21	7.06	6.08	6.16
	6	6.42	7.06	6.51	7.11	6.32	7.09	6.11	6.66
	8	6.79	6 89	6.85	7.23	6.56	7.14	6.31	6.61
	10	6.88	7.22	6.85	7.33	6.44	[1]	6.34	6.51
	16	.....	[1]7.15	7.22	[1]7.33	6.81	[1]7.48	6.52	[1]6.55
	35	.....	7.28	7.44	7.39	6.74	7.36	6.58	6.95
Raw sugar (moisture, official method, 1.22 per cent):	1	0.96	0.87	0.85	0.87	0.96	0.94	0.94	0.86
	2	0.99	0.85	0.94	0.90	0.99	0.98	0.99	0.92
	3	1.05	0.95	0.99	0.96	1.04	0.98	1.03	0.98
	4	1.06	0.99	1.00	0.98	1.06	0.99	1.04	0.99
	5	1.05	0.98	1.01	0.99	1.07	1.00	1.04	1.00
	6	1.04	1.01	0.98	1.00	1.06	1.03	1.03	1.01
	8	1.08	1.03	1.01	1.01	1.07	1.01	1.06	1.02
	10	1.08	1.04	1.01	1.03	1.09	[1]	1.06	1.05
	16	.....	[1]0.99	1.02	[1]1.00	1.07	[1]1.01	1.07	[1]1.01
	35	.....	0.99	0.99	1.01	1.05	0.98	1.05	1.02

[1] Vacuum off.

The dehydration in a partial vacuum did not show in every case the advantage that was expected over the dehydration at atmospheric pressure. On both experiments in drying cheese, from 90 to 94 per cent of the water was dried out in 24 hours in the desiccators held at atmospheric pressure, while in the desiccators at a vacuum of 27 inches, the percentage ran from 93 to 97 per cent of the total moisture in the cheese. On the drying of raw sugar, the vacuum did not appear to be an advantage. Over sulphuric acid, phosphorus pentoxid, and sodium metal the highest results in 24 hours were from the desiccators at atmospheric pressure, while only in the calcium carbid desiccator were the results under vacuum better than those under atmospheric pressure. In drying cocoa and

cornmeal, the vacuum method had a distinct advantage with all the reagents tried.

From the foregoing, it may be seen that dehydration in a partial vacuum is not always more perfect than over the same medium at atmospheric pressure.

A fact that stands out clearly in the experiments is that in a desiccator at room temperature and with atmospheric pressure in 48 hours the materials used for the tests lost from 80 to 96 per cent of all their water and at a pressure of 75 to 100 mm. they lost as much in 24 hours.

The following recommendations are made, therefore, for future work:

RECOMMENDATIONS.

It is recommended—

(1) That comparison of drying organic or other materials at room temperature in partial vacuum and at atmospheric pressure, using phosphorus pentoxid and calcium carbid as dehydrating agents, be continued.

(2) That there be further comparison of the dehydrating power of sulphuric acid, phosphorus pentoxid, calcium carbid, and metallic sodium, and any other reagent that may be found, at room temperature and atmospheric pressure.

(3) That it be ascertained if a general method for moisture may not be used, consisting of 24 or 48 hours storage over either sulphuric acid, phosphorus pentoxid, calcium carbid, or metallic sodium, at room temperature and atmospheric pressure to be followed by the vacuum oven at 70°C. or 100°C. for a short time.

(4) That the moisture determination by vacuum method over sulphuric acid be made an optional official method.

REPORT ON INORGANIC PHOSPHORUS ESTIMATION IN PLANT AND ANIMAL SUBSTANCES.

By E. B. Forbes, *Associate Referee* and A. F. D. Wussow.

This investigation of methods of inorganic phosphorus estimation involved a comparison with animal substances of the neutral molybdate method of Emmett and Grindley, the barium chlorid method of Siegfried and Singewald, and the magnesia mixture method of Forbes and associates; and with plant substances of the acid alcohol method of Forbes and associates and the method of R. C. Collison, likewise founded on the acid-alcohol separation of phytin and inorganic phosphate.

The work was carried through the years 1912 and 1913. Those cooperating with the authors of this report were in 1912 P. F. Trowbridge and A. C. Hogan of the University of Missouri, H. S. Grindley and E. L. Ross of the University of Illinois and H. L. White and R. F. Beard of the

North Dakota Agricultural College; in 1913, H. S. Grindley, C. I. Newlin, P. F. Trowbridge, O. C. Smith, and H. L. White.

The general method of test of the several analytical procedures was by making the estimations with and without the addition of known amounts of inorganic phosphorus, the correctness of the methods being judged from the completeness of recovery of the added phosphate. In the work with plant substances attention was also given to completeness of extraction and the influence of phenol in the extractive reagent.

The main body of this report is made up of the detailed specifications governing the work and the tabular presentation of results of analysis. The discussion of the results will be found on pages 236 to 239.

DETERMINATIONS ON ANIMAL SUBSTANCES, 1912.

Outline showing methods of precipitation, amounts of extracts to be used for each determination, number of determinations, and amount of standard phosphate solution to be added to certain of these determinations; the same set of determinations to be made on muscle, blood and brain:

Muscle Blood Brain (5,000 cc. extract)	Neutral molybdate precipitation (Emmett and Grindley)	a-1	500 cc. of extract.
		a-2	500 cc. of extract.
		a-3	250 cc. of extract + 25 cc. of phosphate solution.
		a-4	250 cc. of extract + 25 cc. of phosphate solution.
	Barium chlorid precipitation (Siegfried and Singewald).	b-1	500 cc. of extract.
		b-2	500 cc. of extract.
		b-3	250 cc. of extract + 25 cc. of phosphate solution.
		b-4	250 cc. of extract + 25 cc. of phosphate solution.
	Magnesia mixture precipitation (Forbes and associates).	c-1	500 cc. of extract.
		c-2	500 cc. of extract.
		c-3	250 cc. of extract + 25 cc. of phosphate solution.
		c-4	250 cc. of extract + 25 cc. of phosphate solution.

PREPARATION OF A COLD WATER EXTRACT OF DESICCATED FLESH.

Weigh out about 45 grams of the vacuum-dried meat, and divide it among sixteen 150 cc. beakers; to each beaker with its contents add about 3 to 5 cc. of distilled water; break up any lumps and stir well with a glass rod until the mass forms a thick paste. Add 50 cc. of distilled water to each beaker and stir thoroughly for 15 minutes; allow the insoluble portion to settle for a few minutes (3 to 5) and decant the supernatant liquid through wet 11 cm. filters; collect the filtrates in 250 cc. Florence flasks; take care that the funnels touch the sides of the necks of the flasks; drain the residues thoroughly, keeping as much of them as possible in the beakers; treat these residues with 25 cc. of distilled water, stirring for 5 to 7 minutes, and then allowing

3 to 5 minutes for the solid particles to settle before filtering. Decant, etc., as just described. Repeat this last treatment until the filtrate measures about 220 cc., then transfer the entire residue to the filter and wash twice with about 8 to 10 cc. of distilled water. Allow all the liquid to pass through the filter before adding the next extract. Whenever the major portion of the residue has become mechanically transferred to the filter, return it to the beaker, using great care not to break the filter paper. Transfer the sixteen filtrates of about 250 cc. each to a measuring flask. Wash out each Florence flask twice, using about 5 to 8 cc. of distilled water each time. Make the extract up to 5,000 cc. and mix it thoroughly without too much mechanical agitation.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BLOOD.

Weigh about 50 grams of fresh blood or its equivalent of oxalated blood into each of six 400 cc. beakers. To each beaker add a few cubic centimeters of distilled water and work up the blood and water with a glass rod; make up to about 200 cc. with boiling distilled water; place over a flame and gradually bring to boiling, with constant stirring. When boiling begins add to each beaker 20 cc. of 20 per cent ammonium sulphate solution; boil with constant stirring for about 10 minutes; decant onto sand on linen. When the liquid is through lift the coagulum off from the sand and return it to a mortar; grind to a smooth paste and transfer from mortar to beaker with boiling distilled water; make up to about 80 cc. with boiling distilled water; stir for 8 minutes and pour contents again onto the sand filter. After the extract is through, return the coagulum to the mortar and grind a second time, transferring to the beaker as before with boiling distilled water. Repeat this process of 8-minute extractions of the coagulum in hot water and filtration as just directed, without further grinding, until the filtrates measure about 750 cc. each. Wash out each beaker twice with 8 to 10 cc. of hot distilled water, completing the transfer of the coagulum and extract to the sand. Wash the coagulum on the sand twice with boiling water from a wash bottle. At all times allow the filter to drain well between additions of extract or wash water. Combine the six filtrates of about 800 cc. each, washing out the containers of each twice with distilled water. Make the extract up to 5,000 cc. and mix.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BRAIN.

Weigh out about 10 grams of brain into each of ten 250 cc. beakers. To each beaker add a few cubic centimeters of distilled water and work up the brain and water with a glass rod; make up to about 100 cc. with boiling water; place over a flame and gradually bring to boiling with constant stirring. After boiling has begun add to each beaker 20 cc. of 20 per cent ammonium sulphate solution; boil for about 10 minutes; allow to settle for a moment and decant liquid onto sand on linen. If the extracts do not filter readily, carefully push the coagulum to one side or return to the beakers. Add to the beakers containing the coagulum 50 cc. of 0.1 per cent ammonium sulphate solution; stir for 1 minute and decant the liquid onto the filter. Repeat this process of one-minute extractions of the coagulum in 0.1 per cent ammonium sulphate solution and filtration as just directed until the filtrates measure about 450 cc. Wash out each beaker twice with 8 to 10 cc. of hot 0.1 per cent ammonium sulphate solution, completing the transfer of the coagulum and extract to the sand. Wash the coagulum twice with the above wash solution from a wash bottle. At all times allow the filter to drain well between additions of extract or wash solution. Combine the ten filtrates, washing out the container of each of the filtrates twice with 5 to 8 cc. of distilled water. Make the extract up to 5,000 cc. and mix.

EMMETT AND GRINDLEY NEUTRAL AMMONIUM MOLYBDATE METHOD FOR INORGANIC PHOSPHORUS IN WATER EXTRACTS OF FLESH.

Measure out the number and volumes of extracts specified in the schedule of determinations. Evaporate with frequent stirring on the water or steam bath to approximately 20 to 25 cc.; while hot, filter into 300 cc. beakers, using doubled 11 cm. No. 589 (Blue Ribbon brand) S. and S. papers. Wash beakers, precipitates, and filters thoroughly with hot water; the volume of the resulting filtrate and washings should be about 125 cc. Add 10 grams of ammonium nitrate and heat upon the water bath to 60°C.; add 10 cc. of nitric acid (specific gravity, 1.20), stir, and add 125 cc. of clear neutral ammonium molybdate solution. (Neutral ammonium molybdate is prepared by adding ammonia to the ordinary molybdic solution, using litmus paper as an indicator. This work should be done very carefully and both red and blue litmus paper used.) Reheat, bringing temperature to 60°C. Keep at this temperature for 15 minutes, stirring vigorously every few minutes. Remove from the bath and allow the solutions to stand 2 hours in a warm place. Decant the clear supernatant liquid through doubled 11 cm. No. 589 (Blue Ribbon brand) S. and S. filters. Transfer the remaining liquid and precipitate to the filters, using a 10 per cent ammonium nitrate solution. Wash precipitates and beakers four or five times with small volumes of the ammonium nitrate solution. Dissolve the yellow precipitate upon the filter and that in the precipitating beaker with dilute ammonium hydroxid (2.5 per cent) and hot water, collecting the filtrate in a 250 cc. beaker; wash thoroughly; neutralize the solution with nitric acid (specific gravity 1.20) and make up to approximately 150 cc.; add 5 grams of ammonium nitrate; heat upon the water bath to 60°C. and then carefully add, while stirring, 5 cc. of concentrated nitric acid and 50 cc. of clear acid molybdic solution. Digest at 60°C. for 15 minutes, stirring occasionally. Continue the determination of phosphorus as usual weighing the phosphorus as magnesium pyrophosphate.

SIEGFRIED AND SINGEWALD METHOD AS USED BY GRINDLEY AND ROSS FOR INORGANIC PHOSPHORUS IN ANIMAL SUBSTANCES.

Measure out the number and volumes of extracts specified in the schedule of determinations. To each portion add 50 cc. of a 10 per cent barium chlorid solution and 10 cc. of a 10 per cent solution of ammonium hydroxid. Stir the solutions every 15 minutes for a period of 1 hour, allow to stand undisturbed for at least 12 hours, and then filter (decanting at first as much as possible) through double quantitative filters. Wash the beakers, precipitates and filters, repeatedly, with small quantities of wash water containing 10 cc. of the barium chlorid solution and 10 cc. of the ammonium hydroxid solution per liter. Place the upper filters containing the precipitates in the beakers in which the precipitation occurred, and digest at room temperature with 35 cc. of dilute nitric acid (specific gravity, 1.20) with frequent stirring. Filter the acid solution through the second filter which was not removed from the funnel, and wash the beakers and filters thoroughly with hot water. Neutralize the filtrates with ammonium hydroxid, slightly acidify with nitric acid, add 10 grams of ammonium nitrate, dilute to about 125 cc., and heat on the water bath to 60°C. Add 100 cc. of acid ammonium molybdate and continue the phosphorus determination as usual.

MAGNESIA MIXTURE METHOD FOR INORGANIC PHOSPHORUS IN EXTRACTS OF ANIMAL TISSUES.

Measure out the number and volumes of extracts specified in the schedule of determinations. Add 10 cc. of magnesia mixture, stirring freely; allow to stand

15 minutes, add 25 cc. of ammonium hydroxid (specific gravity, 0.90); cover and allow to stand overnight.

The next morning filter, and wash the precipitate with 2.5 per cent ammonia water. Dissolve the precipitate on the filter paper with dilute nitric acid into the same beaker in which the first precipitation was made, and wash the papers thoroughly with hot water. Render the resulting solutions nearly neutral; add 5 grams of ammonium nitrate; heat to 65°C.; add 50 cc. of official acid molybdate solution, and keep at 60°C. for 2 hours; continue in the usual way for the gravimetric estimation of phosphorus as the pyrophosphate.

NOTE BY H. S. GRINDLEY.

The extract of the muscle was prepared by the centrifuge method as used in this laboratory rather than by the method as outlined in the directions sent out for the referee work. This was done merely because it was more convenient at the time. The barium chlorid method was not used on the blood because of the presence of the ammonium sulphate. The results on blood are poor on account of some unknown error in our work. We did not feel justified in making up another solution of blood for the repetition of this one determination.

No difficulties other than those usually attending the preparation of solutions of animal tissues were encountered and the details of the procedures connected with the three methods were fairly satisfactory.

DETERMINATIONS ON PLANT SUBSTANCES, 1912.

Corn germ Wheat germ Rice polish Wheat bran	Triplicates on solutions prepared as directed in the following paragraph.	a-10 gram sample. b-10 gram sample. c-10 gram sample.
	Triplicates as above but with 25 cc. of phosphate solution added to each.	a-10 gram sample. b-10 gram sample. c-10 gram sample.

COLLISON METHOD FOR INORGANIC PHOSPHORUS IN PLANT SUBSTANCES.

Weigh out 10-gram portions of the samples in triplicate, and place in 400 cc. Florence flasks, to which add exactly 300 cc. of 94 to 96 per cent phosphorus-free alcohol, containing 0.2 per cent of hydrochloric acid (0.2 per cent actual hydrochloric acid) and close with rubber stopper; shake the flasks at intervals of 5 minutes for 3 hours, and filter through dry double filters into dry flasks; measure out 250 cc. aliquots of the filtrates into 400 cc. beakers; make just alkaline to litmus with ammonium hydroxid and allow to stand for 8 to 12 hours, or overnight. Filter through double filters, and wash with slightly ammoniacal 94 to 96 per cent alcohol. In case a small portion of the precipitate resists transfer from the beaker by the usual means the last traces may be dissolved in 5 drops of hydrochloric acid, with the assistance of a rubber-capped rod. To this acid solution add 10 cc. of alcohol; make slightly alkaline with ammonia, and then transfer to the filter. Wash several times with ammoniacal alcohol; then spread out the inner papers with the precipitates and allow to dry completely. Transfer papers and precipitates to Erlenmeyer flasks containing exactly 100 cc. of 0.5 per cent aqueous solution of nitric acid (0.5 per cent of actual nitric acid). Close the flasks with rubber stoppers; shake until the precipitates are thoroughly broken up, and let stand overnight. Filter through dry double filters into dry beakers; pipette out 75 cc. of each filtrate and determine

TABLE 1.

Test of methods of determination of inorganic phosphorus in animal substances (1912).
(Extracts made up to 5,000 cc.)

SUBSTANCE, METHOD AND DETERMINATION	VOLUME OF EXTRACT USED	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	A. F. D. WUSSOW				P. F. TROWBRIDGE (A. G. HOGAN, ANALYST)			H. S. GRINDLEY AND E. L. ROSS		
			Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added phosphorus recovered as magnesium pyrophosphate[1]		Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added magnesium pyrophosphate recovered[2]	Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added magnesium pyrophosphate recovered[2]
	cc.	*cc.*	*gram*	*per cent*	*gram*	*per cent*	*gram*	*per cent*	*gram*	*gram*	*per cent*	*gram*
Muscle:[3]												
Neutral molybdate method (Emmett and Grindley) a-1	500	0	0.0824	0.5018	......	.....	0.0826	0.5120	......	0.0816	0.4558	......
a-2	500	0	0.0814	0.4956	......	.....	0.0831	0.5150	......	0.0812	0.4535	......
a-3	250	25	0.0814	......	0.0405	.....	0.0812	......	0.0398	0.0828	......	0.0421
a-4	250	25	0.0811	......	0.0402	.....	0.0795	......	0.0381	0.0813	......	0.0406
Average.....	...			0.4987	0.0403	96.2	......		......			
Barium chlorid method (Siegfried and Singewald) b-1	500	0	0.0836	0.5090	......	.....	0.0834	0.5170	......	0.0796	0.4446	......
b-2	500	0	0.0826	0.5029	......	.....	0.0814	0.5040	......	0.0796	0.4446	......
b-3	250	25	0.0850	......	0.0435	.....	0.0831	......	0.0419	0.0802	......	0.0404
b-4	250	25	0.0848	......	0.0433	.....	0.0823	......	0.0411	0.0800	......	0.0402
Average.....				0.5059	0.0434	103.6	......					
Magnesia mixture method (Forbes and associates) c-1	500	0	0.0792	0.4822	......	.....	0.0810	0.5020	......	0.0785	0.4385	......
c-2	500	0	0.0794	0.4834	......	.....	0.0809	0.5010	......	0.0790	0.4413	......
c-3	250	25	0.0798	......	0.0402	.....	0.0816		0.0411	0.0795		0.0401
c-4	250	25	0.0806	......	0.0410	.....	0.0823	......	0.0418	0.0800		0.0406
Average.....					0.0406	96.9	......			......		
Blood:[4]												
Neutral molybdate method a-1	500	0	0.0380	0.0281	......	.....	0.0160	0.0130	......	0.0078	0.0078	......
a-2	500	0	0.0394	0.0292	......	.....	0.0189	0.0150	......	0.0077	0.0077	......
a-3	250	25	0.0568	......	0.0375	.....	0.0490	......	0.0315	0.0447	......	0.0408
a-4	250	25	0.0584	......	0.0391	.....	0.0526	......	0.0351	0.0448	......	0.0409
Average.....				0.0286	0.0383	91.4	......					
Barium chlorid method b-1	500	0	0.0088	0.0065	......	.....	0.0041	0.0033	......	......	......	......
b-2	500	0	0.0094	0.0070	......	.....	0.0041	0.0033	......	......	......	......
b-3	250	25	0.0166	......	0.0121	.....	0.0432	......	0.0412	......	......	......
b-4	250	25	0.0164	......	0.0119	.....	0.0413	......	0.0393	......	......	......
Average.....	...	..	......	0.0067	0.0120	28.6	......	......	......	......	......	......
Magnesia mixture method c-1	500	0	0.0210	0.0156	......	.....	0.0134	0.0110	......	0.0023	0.0023	......
c-2	500	0	0.0212	0.0157	......	.....	0.0133	0.0110	......	0.0007	0.0007	......
c-3	250	25	0.0514	......	0.0409	.....	0.0467	......	0.0400	0.0438	......	0.0431
c-4	250	25	0.0518	......	0.0413	.....	0.0467	......	0.0400	0.0436	......	0.0429
Average.....	...	..	......	0.0156	0.0411	98.1	......	......	......	......	......	......

TABLE 1—Continued.

Brain:[5]													
Neutral molybdate method	a-1	500	0	0.0280	0.0776	......	.....	0.0327	0.0910	...	0.0202	0.0564	......
	a-2	500	0	0.0327	0.0907	......	.....	0.0331	0.0920	.	0.0204	0.0570	......
	a-3	250	25	0.0540	......	0.0237	.....	0.0567	....	0.0402	0.0513	...	0.0412
	a-4	250	25	0.0533	......	0.0230	.....	0.0572	...	0.0107	0.0513	...	0.0412
Average		...	..	......	0.0841	0.0233	55.6	......	.	.	.	...	...
Barium chlorid method	b-1	500	0	0.0034	0.0094	......	.....	0.0057	0.0160	.	.	...	...
	b-2	500	0	0.0038	0.0105	......	.....	0.0060	0.0170		.	...	...
	b-3	250	25	0.0158	......	0.0140	.....	0.0115		0.0086	...	...	...
	b-4	250	25	0.0170	......	0.0152	.....	0.0116	..	0.0087	.....	...	.....
Average		...		......	0.0099	0.0146	34.6	......		..	.	...	...
Magnesia mixture method	c-1	500		0.0216	0.0599	......	.....	0.0320	0.0890	....	0.0189	0.0528	......
	c-2	500		0.0210	0.0582	......	.....	0.0303	0.0840		0.0193	0.0539	
	c-3	250		0.0498	......	0.0392	.....	0.0570	..	0.0414	0.0512	..	0.0417
	c-4	250	25	0.0507	......	0.0401	...	0.0572	...	0.0416	0.0510	..	0.0415
Average	.	...	..	....	0.0590	0.0396	94.5	......	..	...	...	....	.....
Phosphate solution:													
Neutral molybdate method	1		25	0.0424	.	.	.		...	...	.	...	......
	2	...	25	0.0426	......	......	.		.	.	.	...	.....
	3	...	25	0.0424	....	...			.	..	.	...	...
Average	.	...		0.0425	.	..	.		.	..	...	...	....
Barium chlorid method	1	...	25	0.0420	......	......	.....	.....	.	..	....	......	......
	2	...	25	0.0424	......	......	.....	......	.	.	...	..	......
	3	...	25	0.0422	......	......	.....	...	...	....	....	...	......
Average	.	...		0.0423	.....	...	...		...	....	....	...	...
Magnesia mixture method	1	...	25	0.0422	......	......	...	....	...	....	......	......	......
	2	...	25	0.0421	......	......	.....	.	...	.	...	......	......
	3	...	25	0.0419	....	.	.	.	..	....	.....	......	......
Average	.	...	..	0.0421	...	...	...	...	...	...	......	......	......
Direct precipitation with magnesia mixture	1	...	25	0.0420	.....	....	....	....	...	.....	......	.....	......
	2	...	25	0.0418	......	......	.....	......	....	....	.....	......	......
	3	...	25	0.0420	......	......	.....	......	.....	.....	......	......	......
Average		...	..	0.0419	......	......	.....	.....	......	......	......	......	......

[1] Should have been about 0.0419 gram.
[2] Should have been about 0.0410 gram.
[3] Muscle used by Wussow was vacuum dried, 45.7822 grams; by Trowbridge, vacuum dried, 45 grams; by Grindley and Ross, vacuum dried, 50 grams.
[4] Blood used by Wussow, fresh pig, 376.2846 grams; by Trowbridge, 5 days old calf, 349.2022 grams; by Grindley and Ross, 300 grams of oxalated blood corresponding to 280.9 grams of fresh blood.
[5] Brain used by Wussow, fresh calf, 100.5238 grams; by Trowbridge, 5 days old calf, 100 grams; by Grindley and Ross, 100 grams.

TABLE 2.

Test of methods of determination of inorganic phosphorus in plant substances (1912).

SUBSTANCE	A. F. D. WUSSOW[1]								H. S. GRINDLEY AND E. L. ROSS			H. L. WHITE					P. F. TROWBRIDGE (A. G. HOGAN, ANALYST)				
		FIRST EXTRACTION			SECOND EXTRACTION																
							Excess of phosphorus extracted[3]														
	Sample	Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added phosphorus recovered as magnesium pyrophosphate[2]	Magnesium pyrophosphate obtained		Magnesium pyrophosphate	Percentage of sample	Sample	Magnesium pyrophosphate obtained	Phosphorus obtained	Sample	Phosphate solution added	Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added magnesium pyrophosphate recovered[4]	Sample	Phosphate solution added	Magnesium pyrophosphate obtained	Inorganic phosphorus obtained	Added magnesium pyrophosphate recovered[4]
		gram	*per cent*	*gram*	*per cent*	*gram*	*gram*			*gram*	*per cent*		*cc.*	*gram*	*per cent*	*gram*		*cc.*	*gram*	*per cent*	*gram*
Corn germ	1	0.0066	0.0294	...	...	0.0026	0.0015	0.0067	a	0.0055	0.0245	a	0	0.0056	0.025	...	a	0	0.0075	0.0336	...
	2	0.0068	0.0303	...	...	0.0024	0.0013	0.0058	b	0.0062	0.0276	b	0	0.0059		...	b	0	0.0063	0.0288	...
	3	0.0065	0.0290	...	...	0.0025	0.0014	0.0062	c	0.0056	0.0249	c	25	0.0178	...	0.0120	c	0	0.0052	0.0224	...
	4	0.0176	...	0.0110	...	0.0042	0.0013	...	...	...	...	d	25	0.0185	...	0.0127	d	25	0.0174	...	0.0111
	5	...	...	...	...	0.0042	...	...	...	...	...	e	25	0.0172	...	0.0114	e	25	0.0165	...	0.0102
	6	0.0178	...	0.0112	...	0.0043	0.0013	...	...	...	...	...	...	...	...	...	f	25	0.0168	...	0.0105
Average	...	...	0.0299	0.0111	95.7	...	...	0.0062	...	...	0.0257	...	...	...	...	...	...	...	...	...	...
Wheat germ	1	0.0090	0.0401	...	...	0.0040	0.0025	0.0111	a	0.0080	0.0356	a	0	0.0082	0.036		a	0	0.0088	0.0400	...
	2	0.0091	0.0406	...	...	0.0037	0.0022	0.0098	b	0.0076	0.0338	b	0	0.0080		...	b	0	0.0074	0.0336	...
	3	0.0090	0.0401	...	...	0.0048	0.0033	0.0147	c	0.0076	0.0338	c	25	0.0216	...	0.0135	c	0	0.0078	0.0352	...
	4	0.0204	...	0.0114	...	0.0071	0.0037	...	...	...	...	d	25	0.0196	...	0.0115	d	25	0.0193	...	0.0113
	5	0.0206	...	0.0116	...	0.0070	0.0036	...	...	...	...	e	25	0.0203	...	0.0122	e	25	0.0156	...	0.0076
	6	0.0204	...	0.0114	...	0.0068	0.0034	...	...	...	...	f	25	0.0188	...	0.0107	...	...	...	...	...
		...	...	...		...	...	...	...	...	...	g	25	0.0198	...	0.0117	...	...	...	...	...
Average		...	0.0403	0.0115	99.1	...	...	0.0119	...	...	0.0343	...	...	...	...	...	...	...	...	...	...
Rice polish	1	0.0047	0.0210	...	...	0.0020	0.0012	0.0053	a	0.0037	0.0165	a	0	0.0042	0.020	...	a	0	0.0125	0.0560	...
	2	0.0048	0.0214	...	...	0.0018	0.0010	0.0045	b	0.0037	0.0165	b	0	0.0048		...	b	0	...	...	...
	3	0.0048	0.0214	...	...	0.0022	0.0014	0.0062	c	0.0036	0.0160	c	25	0.0154	...	0.0109	c	0	0.0034	0.0144	...
	4	0.0154	...	0.0106	...	0.0038	0.0012	...	...	...	...	d	25	0.0150	...	0.0105	d	25	0.0155	...	0.0121
	5	0.0158	...	0.0110	...	...	...	...	...	...	...	e	25	0.0160	...	0.0115	e	25	0.0162	...	0.0128
	6	0.0160	...	0.0112	...	0.0042	0.0015	...	...	...	...	...	...		...	...	f	25	0.0150	...	0.0116
Average	...	...	0.0213	0.0109	94.0	...	...	0.0053	...	...	0.0163	...	...	...	...	...	...	...	...	...	...
Wheat bran	1	0.0088	0.0392	...	...	0.0040	0.0025	0.0111	a	0.0078	0.0347	a	0	0.0074		...	a	0	0.0061	0.0272	...
	2	0.0084	0.0375	...	...	0.0042	0.0028	0.0125	b	0.0076	0.0338	b	0	0.0080	0.034	...	b	0	0.0068	0.0304	...
	3	0.0084	0.0375	...	...	0.0042	0.0028	0.0125	c	0.0073	0.0325	c	0	0.0080		...	c	0	0.0068	0.0304	...
	4	0.0182	...	0.0097	...	0.0064	0.0034	...	...	...	...	d	25	0.0190	...	0.0112	d	25	0.0178	...	0.0112
	5	0.0189	...	0.0104	...	0.0069	0.0038	...	...	...	...	e	25	0.0200	...	0.0122	e	25	0.0150	...	0.0084
	6	0.0184	...	0.0099	...	0.0060	0.0030	...	...	...	...	f	25	0.0192	...	0.0114	f	25	0.0142	...	0.0076
Average	...	...	0.0381	0.0100	86.2	...	...	0.0120	...	...	0.0337	...	...	...	...	...	...	...	...	...	...

[1] Phosphate solution precipitated directly with magnesia mixture in 25 cc. gave in Sample 1, 0.0186 gram of phosphorus; Sample 2, 0.0186 gram; Sample 3, 0.0182 gram; average 0.0185 gram. The blank in each case gave 0.0004 gram of phosphorus.

[2] Should have been about 0.0116 gram.

[3] Phosphorus in excess of quantity which should be obtained, after making allowances for quantity left in aliquot not taken in regular determination.

[4] Should have been about 0.0133 gram.

phosphorus in the usual way, precipitating first with acid molybdate solution, then with magnesia mixture, and weigh as the pyrophosphate.

If the final solutions are highly colored, dissolve the pyrophosphates and reprecipitate.

NOTE BY H. S. GRINDLEY AND E. L. ROSS.

The details of procedure worked satisfactorily. It seems to us that if possible the weights of magnesium pyrophosphate should be increased in order to insure more reliable final results.

We regret to say that as a result of a number of experiments we are convinced that the acid alcohol method as outlined does not insure complete extraction of all the inorganic phosphorus from meals, or the solvent gradually converts the organic forms of phosphorus into the inorganic form. A second and a third extraction of the samples with the 0.2 per cent acid-alcohol, after making the proper corrections in each case for the aliquot portion from the former extracts, gave additional inorganic phosphorus. The second extraction gave the following percentages of phosphorus: Corn germ, 0.0052; wheat germ, 0.0012; rice polish, 0.0018; and wheat bran, 0.0011. Proceeding in a similar manner the third extract gave the following percentages of phosphorus: Corn germ, 0.0004; wheat germ 0.0032; rice polish 0.0035; and wheat bran 0.0029. It thus seems that the third extract apparently contained more organic phosphorus expressed as per cent than did the second extract. This is probably accounted for by the fact that the filtration of the acid alcohol for the third determination was made during the middle of a very hot day and the filtration proceeded slowly so that a considerable loss of alcohol by volatilization resulted. In fact we were unable to get the usual 250 cc. portions from the filtrates and had to take only 200 cc. for each determination. This loss of alcohol by evaporation would result in giving higher results than should be obtained. Other tests of a similar nature gave similar results.

Further, dipotassium hydrogen phosphate deposited as a solid in the tissue of filter paper apparently cannot be completely extracted by 300 cc. of 0.2 per cent acid alcohol under conditions such as those now used in this method for the solution, separation, and estimation of phosphorus in vegetable substances.

DETERMINATIONS ON ANIMAL SUBSTANCES, 1913.

Muscle Blood Brain	*A*. Extract of samples as weighed.	a-1	Neutral molybdate precipitation.
		a-2	Neutral molybdate precipitation.
		a-3	Neutral molybdate precipitation.
		a-4	Magnesia mixture precipitation.
		a-5	Magnesia mixture precipitation.
		a-6	Magnesia mixture precipitation.
	B. Extract of samples as weighed plus 25 cc. of phosphate solution.	b-1	Neutral molybdate precipitation.
		b-2	Neutral molybdate precipitation.
		b-3	Neutral molybdate precipitation.
		b-4	Magnesia mixture precipitation.
		b-5	Magnesia mixture precipitation.
		b-6	Magnesia mixture precipitation.

Determine by both methods of precipitation the phosphorus in the phosphate solution used; also make blank determinations in triplicate on reagents.

PREPARATION OF COLD WATER EXTRACT OF MUSCLE.

A. Weigh out 10 to 12 grams of fresh muscle and divide as nearly equally as possible between two small beakers; moisten the samples with a few cubic centimeters of distilled water, and break up lumps with a glass rod; add 50 cc. of water to each beaker and stir contents for 15 minutes. Allow insoluble residue to settle for 3 to 5 minutes, then decant the liquid from each beaker through filters into beakers; allow to drain and add 25 cc. of water; stir for 7 to 8 minutes, and after allowing to settle, decant onto the same filter. Continue this treatment, using each time 25 cc. of water, until the filtrates measure about 230 cc. each. Allow the filters to drain completely between extractions. Whenever the major portion of the residue has become mechanically transferred to the filter return it to the beaker, using great care not to break the filter paper. After the last extraction throw the entire contents of each beaker onto the filter, and after draining, wash twice with small quantities of distilled water. Combine the two extracts, and use for the precipitation of the phosphates under Section *A*.

B. Weigh out same quantity of flesh as specified for A, and divide as nearly equally as possible between two small beakers: work up with a few cubic centimeters of distilled water; add 25 cc. of aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate, dividing as nearly equally as possible between the two beakers and proceed as directed under A. The extract thus obtained is ready for precipitation under *B*.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BLOOD.

A. Weigh out 30 to 35 grams of fresh blood, or the equivalent of oxalated blood, into a 400 cc. beaker; add a few cubic centimeters of distilled water, and work up the blood and water with a glass rod; make up to about 150 cc. with boiling distilled water; place over a flame, and gradually bring to boiling, with constant stirring. When boiling begins add 20 cc. of 20 per cent ammonium sulphate solution. Boil with constant stirring, for about 10 minutes; decant onto a filter of sand on linen, receiving the filtrate in an 800 cc. beaker. When the liquid is through, lift the coagulum from the sand, and transfer it to a mortar; grind to a smooth paste and transfer from mortar to beaker with boiling distilled water; make up to about 50 cc. with the same; stir for 8 minutes, and pour contents again onto the sand filter. After the extract is through, return the coagulum to the mortar, and grind a second time, transferring to the beaker as before with boiling distilled water. Repeat this process of 8-minute extractions of the coagulum in hot water, and filtration as just directed, without further grinding, until the filtrate measures about 450 cc. Wash out each beaker twice with 8 to 10 cc. of hot water, completing the transfer of the coagulum and extract to the sand. Wash the coagulum on the sand twice with boiling water from a wash bottle. At all times allow the filter to drain well between additions of extract or wash water. This extract of about 500 cc. is ready for precipitation under Section *A*.

B. Weigh out same quantity of blood as specified for A. Work up with a few cubic centimeters of distilled water; add 25 cc. of an aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate and proceed as directed under A. The extract thus obtained is ready for precipitation under *B*.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BRAIN.

A. Weigh out about 10 grams of brain into a 250 cc. beaker; add a few cubic centimeters of distilled water and work up the brain and water with a glass rod; make up

to about 100 cc. with boiling water, place over a flame, and gradually bring to boiling with constant stirring. After boiling has begun add 20 cc. of 20 per cent ammonium sulphate solution; boil gently for about 10 minutes; allow to settle for a moment, and decant liquid slowly onto a filter of sand on linen,[1] receiving the extract in an 800 cc. beaker. Add to the beaker containing the coagulum 50 cc. of a 0.1 per cent ammonium sulphate solution; stir for 1 minute, keeping over flame and at the boiling point; decant the liquid onto the filter. Repeat this process of 1 minute extractions of the coagulum in 0.1 per cent ammonium sulphate solution, and filtration as directed, until the filtrate measures about 450 cc. Wash out the beaker twice with 8 to 10 cc. of hot 0.1 per cent ammonium sulphate solution, completing the transfer of the coagulum and extract to the sand. Wash the coagulum twice with the above wash solution from a wash bottle. At all times allow the filter to drain well between additions of extract or wash solution. This extract of about 500 cc. is ready for precipitation under *A*.

B. Weigh out same quantity of brain as specified for A; work up with a few cubic centimeters of distilled water; add 25 cc. of an aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate and proceed as directed under A. The extract thus obtained is ready for precipitation under *B*.

NEUTRAL AMMONIUM MOLYBDATE METHOD FOR INORGANIC PHOSPHORUS IN WATER EXTRACTS OF FLESH.

Treat 3 of the extracts prepared according to the directions for A, and 3 of those prepared as for B as follows: Evaporate, with frequent stirring on the water or steam bath, to approximately 20 to 25 cc.; while hot, filter into 300 cc. beakers, using doubled 11 cm. S. and S. No. 589 "Blue Ribbon" papers. Wash beakers, precipitates and filters thoroughly with hot water. The volume of the resulting filtrate and washings should be about 125 cc. Add 10 grams of ammonium nitrate and heat upon the water bath to 60°C. Then add 10 cc. of nitric acid (specific gravity, 1.20), stir, and add 125 cc. of clear neutral molybdic solution. (Neutral ammonium molybdate is prepared by adding ammonia to the ordinary molybdic solution, using litmus paper as an indicator. This work should be done very carefully and both red and blue litmus paper used.) Reheat, bringing temperature to 60°C.; keep at this temperature for 15 minutes; stir vigorously every few minutes during this time. Remove from the bath and allow the solutions to stand 2 hours in a warm place. Decant the clear supernatant liquid through doubled 11 cm. No. 589 (Blue Ribbon brand) S. and S. filters. Transfer the remaining liquid and precipitate to the filters, using a 10 per cent ammonium nitrate solution. Wash precipitates and beakers four or five times with small volumes of the ammonium nitrate solution. Dissolve the yellow precipitate upon the filter and that in the precipitating beaker with dilute ammonium hydroxid (2.5 per cent) and hot water, collecting the filtrate in a 250 cc. beaker. Wash thoroughly; neutralize the solution with nitric acid (specific gravity, 1.20) and make up to approximately 150 cc.; add 5 grams of ammonium nitrate; heat upon the water bath to 60°C. and then carefully add, while stirring 5 cc. of concentrated nitric acid and 50 cc. of clear acid molybdic solution. Digest at 60°C. for 15 minutes, stirring occasionally. Continue the determination of phosphorus as usual weighing the phosphorus as magnesium pyrophosphate.

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[1] It is desirable to prevent the extract or coagulum from coming in contact with the linen before passing through the sand. To this end pour extract slowly onto center of sand or into a cup-shaped depression.

MAGNESIA MIXTURE METHOD FOR INORGANIC PHOSPHORUS IN EXTRACTS OF ANIMAL TISSUES.

Treat 3 of the extracts prepared according to the directions for *A*, and 3 of those prepared as for *B* as follows: Add 10 cc. magnesia mixture, stirring freely; allow to stand 15 minutes; add 25 cc. of ammonium hydroxid (specific gravity 0.90); cover, and allow to stand overnight. The next morning filter and wash the precipitate with 2.5 per cent ammonia water. Dissolve the precipitate on the filter paper and that remaining in the beaker in which the precipitation was made with dilute nitric acid (1 : 1) and hot water, receiving the solution in 400 cc. beakers. Neutralize the nitric acid with ammonium hydroxid; make slightly acid with nitric acid. Add 5 grams of ammonium nitrate, and precipitate in the usual way with molybdate solution. Continue in the usual way for the gravimetric estimation of phosphorus as the pyrophosphate.

Blanks and phosphorus estimations on phosphate solutions used in work reported in the preceding table.

SAMPLE	SOLUTIONS	MAGNESIUM PYROPHOSPHATE
		gram
Blood:	Blank 1: Neutral molybdate precipitation	0.0020
	Blank 2: do	0.0016
	Blank 3: do	0.0018
	Average	0.0018
	Blank 4: Magnesia mixture precipitation	0.0030
	Blank 5: do	0.0037
	Blank 6: do	0.0038
	Average	0.0035
Brain:	Blank 7: Magnesia mixture precipitation	0.0010
	Blank 8: do	0.0010
	Blank 9: do	0.0006
	Average	0.0009
Blood and muscle:	Phosphate solution 1: Neutral molybdate precipitation 25 cc.	0.0419
	Phosphate solution 2: do 25 cc.	0.0416
	Phosphate solution 3: do 25 cc.	0.0418
	Average	0.0418
	Phosphate solution 4: Magnesia mixture precipitation 25 cc.	0.0417
	Phosphate solution 5: do 25 cc.	0.0415
	Phosphate solution 6: do 25 cc.	0.0411
	Average	0.0414
	Phosphate solution 7: Direct precipitation with magnesia mixture 25 cc.	0.0413
	Phosphate solution 8: do 25 cc.	0.0419
	Phosphate solution 9: do 25 cc.	0.0419
	Average	0.0417
Brain:[1]	Phosphate solution 10: Direct precipitation with magnesia mixture 50 cc.	0.0266
	Phosphate solution 11: do 50 cc.	0.0269
	Phosphate solution 12: do 50 cc.	0.0264
	Average	0.0266
	Phosphate solution 13: 50 cc. diluted to 500 cc.: $16\frac{2}{3}$ grams ammonium sulphate added	0.0264
	Phosphate solution 14: do	0.0262
	Phosphate solution 15: do	0.0267
	Average	0.0264

[1] For modification of method used with brain see p. 236.

RESULTS ON ANIMAL SUBSTANCES, 1913.

TABLE 3.

Test of methods of determination of inorganic phosphorus in animal substances, 1913.

(Analyses by A. F. D. Wussow.)

SUBSTANCE, METHOD AND DETERMINATION	WEIGHT OF SAMPLE	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	MAGNESIUM PYROPHOSPHATE OBTAINED	INORGANIC PHOSPHORUS OBTAINED	ADDED PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
	grams	*gram*	*gram*	*per cent*	*gram*	*per cent*
Muscle:						
Neutral molybdate method.	a-1 13.5485	......	0.0276	0.0568	......	....
	a-2 11.5760	......	0.0240	0.0578	......	....
	a-3 13.3025	......	0.0259	0.0543	......	....
Average...............	......	......	......	0.0563	......	....
	b-1 11.9395	......	0.0648	......	0.0407	....
	b-2 11.5370	......	0.0636	......	0.0403	....
	b-3 12.6880	......	0.0654	......	0.0398	....
Average...............	......	0.0417	......	......	0.0403	96.6
Magnesia mixture method.	a-4 14.5075	......	0.0303	0.0582	......	....
	a-5 10.0850	......	0.0219	0.0605	......	....
	a-6 11.4130	......	0.0229	0.0559	......	....
Average...............	......	......	......	0.0582	......	....
	b-4 11.7065	......	0.0617	......	0.0373	....
	b-5 11.3530	......	0.0606	......	0.0369	....
	b-6 12.1045	......	0.0621	......	0.0368	....
Average...............	......	0.0417	......	......	0.0370	88.7
Blood:						
Neutral molybdate method.	a-1 29.1950	......	[1]0.0324	0.0309	......	....
	a-2 35.0955	......	[1]0.0359	0.0285	......	....
	a-3 28.4170	......	[1]0.0257	0.0252	......	....
Average...............	......	......	......	0.0282	......	....
	b-1 36.5820	......	[1]0.0718	......	0.0348	....
	b-2 27.3368	......	[1]0.0662	......	0.0385	....
	b-3 32.8275	......	[1]0.0699	......	0.0367	....
Average...............	......	0.0417	......	......	0.0367	88.0
Magnesia mixture method.	a-4 30.9601	......	[1]0.0157	0.0141	......	....
	a-5 32.4669	......	[1]0.0146	0.0125	......	....
	a-6 29.2820	......	[1]0.0151	0.0144	......	....
Average...............	......	......	......	0.0137	......	....
	b-4 35.6872	......	[1]0.0545	......	0.0370	....
	b-5 35.2757	......	[1]0.0565	......	0.0392	....
	b-6 36.1812	......	[1]0.0532	......	0.0354	....
Average...............	......	0.0417	......	......	0.0372	89.2
Brain:[2]						
Magnesia mixture method.	a-4 10.1650	......	[1]0.0246	0.0675	......	....
	a-5 10.3040	......	[1]0.0251	0.0679	......	....
	a-6 10.9550	......	[1]0.0267	0.0679	......	....
Average...............	......	......	......	0.0678	......	....
	b-4 10.5095	0.0266	[1]0.0512	......	0.0257	....
	b-5 9.2880	0.0266	[1]0.0483	......	0.0257	....
	b-6 10.5465	0.0266	[1]0.0514	......	0.0258	....
Average...............	......	0.0266	......	......	0.0257	96.6

[1] Blanks deducted.

[2] For modification of method used with brain see p. 236.

TABLE 4.

Determination of inorganic phosphorus in pig's blood extracted with 3⅓ per cent ammonium sulphate solution (each extract about 500 cc.)

(Analyses by A. F. D. Wussow.)

DETERMINATION	WEIGHT OF SAMPLE TAKEN	TREATMENT OF EXTRACT	MAGNESIUM PYROPHOSPHATE OBTAINED	INORGANIC PHOSPHORUS
	grams		*gram*	*per cent*
1	33.0990	Evaporated, boiled, and filtered	0.0217	0.0183
2	34.4230	do	0.0222	0.0180
Average	......		......	0.0180
3	33.3960	Evaporated and filtered	0.0216	0.0180
4	31.3340	do	0.0218	0.0194
Average	......		......	0.0187
5	33.7026	Precipitated directly	0.0108	0.0089
6	33.2960	do	0.0108	0.0090
Average	......		......	0.0089

TABLE 5.

Inorganic phosphorus in brain determined by modified method.

(Analyses by F. M. Beegle.)

SUBSTANCE, METHOD, AND DETERMINATION	WEIGHT OF SAMPLE TAKEN	MAGNESIUM PYROPHOSPHATE OBTAINED	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	ADDED PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
	grams	*gram*	*per cent*	*gram*	*gram*	*per cent*
Brain:[1]						
Magnesia mixture method a–4	7.7011	[2]0.0176	0.06623	......	......	....
a–5	9.2368	[2]0.0209	0.06518	......	......	....
b–4	10.7215	[2]0.0507	......	0.0267	0.0263	....
b–5	9.2277	[2]0.0474	......	0.0267	0.0264	....
b–6	10.5182	[2]0.0502	......	0.0267	0.0263	....
Average	......	......	......	0.0267	0.0263	98.9
Phosphate solution (50 cc.):						
1	......	0.0266	......	......	......	....
2	......	0.0269	......	......	......	....
3	......	0.0265	......	......	......	....
Average	......	0.0267	......	......	......	....
Blank:						
1	......	0.0008	......	......	......	....
2	......	0.0006	......	......	......	....
3	......	0.0008	......	......	......	....
Average	......	0.0007	......	......	......	....

[1] For changed details of method followed see p. 236.
[2] Blanks deducted.

DETERMINATIONS ON PLANT SUBSTANCES, 1913.

Bluegrass Alfalfa Rice polish Brewer's grains	Triplicates on solutions prepared as directed in following section	a-1 10 gram samples. a-2 10 gram samples. a-3 10 gram samples. b-1 10 gram samples—50 cc. of phosphate solution B. b-2 10 gram samples—50 cc. of phosphate solution B. b-3 10 gram samples—50 cc. of phosphate solution B.
	Triplicates on solutions prepared as directed on page 232 (aqueous hydrochloric acid-phenol extract)	c-1 10 gram samples. c-2 10 gram samples. c-3 10 gram samples. d-1 10 gram samples—50 cc. of phosphate solution D. d-2 10 gram samples—50 cc. of phosphate solution D. d-3 10 gram samples—50 cc. of phosphate solution D.

Determine strength of phosphate solutions B and D; also make blank determinations in triplicate on reagents.

A. AQUEOUS HYDROCHLORIC ACID EXTRACTION.

Pour exactly 300 cc. of 0.2 per cent hydrochloric acid (4.6 cc. of concentrated hydrochloric acid, specific gravity 1.18 to 1.19, per liter) onto 10 grams of sample in a dry 400 cc. Florence flask. Close with rubber stopper, and shake at intervals of 5 minutes for 3 hours. Filter the extract by suction into dry flasks through S. and S. No. 589 "Blue Ribbon" papers, in a Witt filtering apparatus, or a Büchner funnel.

Measure out a 250 cc. portion of this filtered extract, and precipitate in a 400 cc. beaker with 10 cc. of magnesia mixture and 20 cc. of ammonium hydroxid (specific gravity 0.9). Allow to stand overnight, and filter through double S. and S. No. 589 "White Ribbon" papers, taking care to decant as long as possible without pouring out the precipitate. Then complete the transfer of the precipitate to the paper.

Wash three times with 2.5 per cent ammonium hydroxid, and then three times with 95 per cent alcohol. Allow the precipitate to drain, spread out the inner paper on the top of the funnel, and allow the alcohol to evaporate. When practically dry, place this inner paper with the precipitate into an Erlenmeyer flask; add 100 cc. of 95 per cent alcohol containing 0.2 per cent of nitric acid; close the flask with a rubber stopper and shake vigorously until the paper is thoroughly broken up. If the precipitate is flaky, and refuses to break up on shaking, allow to stand in the acid-alcohol overnight. Filter through a dry filter into a dry flask; pipette out 75 cc. of the filtrate into a small beaker, and evaporate almost but not quite to dryness. Dissolve in dilute nitric acid, and filter if necessary; then determine phosphorus in the usual gravimetric way, by precipitation first with acid molybdate solution, later with magnesia mixture, and then by burning to the pyrophosphate.

The result obtained represents 6.25 grams out of the original 10 grams of material and so to reduce to a 1-gram basis multiply by 0.16.

B. AQUEOUS HYDROCHLORIC ACID EXTRACTION PLUS PHOSPHATE.

Proceed as under A except that in place of 300 cc. of 0.2 per cent hydrochloric acid add 250 cc. of the same and 50 cc. of phosphate solution containing disodium phosphate equivalent to approximately 25 mg. of magnesium pyrophosphate per 50 cc. Make up this phosphate solution with 0.2 per cent hydrochloric acid.

C. AQUEOUS HYDROCHLORIC ACID-PHENOL EXTRACTION.

Proceed as under A except that in place of 300 cc. of 0.2 per cent hydrochloric acid add 300 cc. of 0.2 per cent hydrochloric acid solution containing 50 grams of phenol per liter.

D. AQUEOUS HYDROCHLORIC ACID-PHENOL EXTRACTION PLUS PHOSPHATE.

Proceed as under C except that in place of 300 cc. add 250 cc. of 0.2 per cent hydrochloric acid containing 50 grams of phenol per liter and 50 cc. of phosphate solution containing disodium phosphate equivalent to approximately 25 mg. of magnesium pyrophosphate per 50 cc. Make up this phosphate solution with 0.2 per cent hydrochloric acid containing 50 grams of phenol per liter.

NOTE: Make phosphate solutions used in B and D of same strength by weighing out equal quantities of the phosphate, and determine their exact strength by precipitating in triplicate 50 cc. with magnesia mixture, filtering, igniting, and weighing direct.

Make blank determinations in triplicate on reagents.

RESULTS ON PLANT SUBSTANCES, 1913.

Blanks on solutions used in work reported in Table 6.

SOLUTION	GRAMS OF MAGNESIUM PYROPHOSPHATE			
	Wussow[1]	Grindley and Newlin	White	Trowbridge and Smith
Blank 1: Aqueous hydrochloric acid solutions	0.0002	0.0012	0.0000	0.0011
2: do	0.0002	0.0012	0.0000	0.0011
3: do	0.0002	0.0006	0.0000	0.0007
Average	0.0002	0.0010	0.0000	0.0009
Blank 1: Aqueous hydrochloric acid phenol solutions	0.0002	0.0161	......	0.0000
2: do	0.0002	0.0159	......	0.0002
3: do	0.0002	0.0163	......	0.0004
Average	0.0002	0.0161	......	0.0002
Phosphate solution 1: (Aqueous hydrochloric acid) 50 cc.	0.0250	0.0005	0.0426	0.0139
2: do	0.0248	0.0012	0.0456	0.0135
3: do	0.0248	0.0012	0.0432	0.0130
Average	0.0249	0.0010	0.0438	0.0134
Phosphate solution 1: (Aqueous hydrochloric acid phenol) 50 cc.	0.0249	0.0152	......	0.0136
2: do	0.0249	0.0157	......	0.0135
3: do	0.0249	Lost	......	0.0125
Average	0.0249	0.0155	......	0.0132

[1] In the second set of determinations with alfalfa, magnesium precipitates were allowed to stand an extra day before filtering, and, after filtering, an extra day in acid alcohol; with Samples a-1 and a-3 only 200 cc. of aqueous hydrochloric acid extract was used, but figures given represent 250 cc. as usual. With blue grass in Samples a-1, a-2, and a-3, only 200 cc. of the aqueous hydrochloric acid extract were used, but weights given for magnesium pyrophosphate represent 250 cc. With rice polish, magnesium precipitate was broken up in acid alcohol with stirring rod before filtering off 75 cc. of aliquot.

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[1] Should have been about 0.0153 gram.

[2] Not included in the average.

[3] In the second extraction 200 cc. instead of 250 cc. of the aliquot were used.

TABLE 6

Test of methods of determination of inorganic phosphorus in plant substances (1913).

Substance, method and determination		A. F. D. Wussow								B. S. Grindley and C. I. Newlin				H. L. White			P. F. Trowbridge and O. C. Smith[1]		
		Magnesium pyrophosphate obtained		Inorganic phosphorus		Added phosphorus recovered as magnesium pyrophosphate[3]				Magnesium pyrophosphate obtained	Inorganic phosphorus	Added phosphorus recovered as magnesium pyrophosphate[3]		Magnesium pyrophosphate obtained	Inorganic phosphorus	Added phosphorus recovered as magnesium pyrophosphate[4]	Magnesium pyrophosphate obtained	Inorganic phosphorus	Added phosphorus recovered as magnesium pyrophosphate[5]
		First set of determinations	Second set of determinations	First set of determinations	Second set of determinations	First set of determinations		Second set of determinations											
		gram	gram	per cent	per cent	gram	per cent	gram	per cent	gram	per cent	gram	per cent	gram	per cent	gram	gram	per cent	gram
[illegible]																			
Aqueous hydrochloric acid extraction	a 1	0.0189	0.0219							0.0136	0.0608	0		0.0206	0.0916		[6]0.0063	[6]0.028	
	a 2	0.0170	0.0184							0.0157	0.0702	0		0.0218	0.0969		0.0208	0.093	
	a 3		0.0160							0.0178	0.0795	0		0.0214	0.0951		0.0202	0.090	
Average		0.0180	0.0188	0.0803	0.0838					0.0157	0.0702	0		0.0212	0.0945		0.0205	0.092	
	b 1	0.0188	0.0237							0.0256		0.0099		0.0444		0.0232	0.0284	0.127	
	b 2	0.0222								0.0320		0.0163		0.0446		0.0234	0.0305	0.136	
	b 3	0.0225	0.0235							0.0290		0.0133		0.0444		0.0232	0.0284	0.127	
Average		0.0212	0.0236			0.0032	20.5	0.0048	30.8	0.0289		0.0132	85.7	0.0444		0.0232	0.0291	0.130	0.0080
Aqueous hydrochloric acid-phenol extraction	c 1	0.0182	0.0140							0.0134	0.0599	0		[7]0.0138	0.0613		0.0237	0.106	
	c-2	0.0168	0.0189							0.0152	0.0679	0		[7]0.0178	0.0791		0.0225	0.100	
	c 3	0.0175	0.0149							0.0101	0.0451	0		[7]0.0206	0.0916		0.0224	0.100	
Average		0.0175	0.0159	0.0780	0.0709					0.0129	0.0576	0		0.0174	0.0740		0.0229	0.102	
	d 1	0.0210	0.0232							0.0204		0.0075		[7]0.0428			0.0300	0.114	
	d 2	0.0203	0.0241							0.0257		0.0128		[7]0.0422			0.0292	0.130	
	d 3	0.0229								0.0205		0.0076		Lost			0.0301	0.134	
Average		0.0213	0.0236			0.0038	24.3	0.0077	49.3	0.0222		0.0093	60.4				0.0298	0.133	0.0009
[illegible]																			
Aqueous hydrochloric acid extraction	a 1	0.0228	0.0380							0.0414	0.1850	0		0.0480			0.0458	0.204	
	a 2	0.0225	0.0379							0.0356	0.1591	0		0.0472			0.0436	0.194	
	a 3	0.0224	0.0335							0.0335	0.1765	0		0.0458			0.0433	0.193	
Average		0.0226	0.0365	0.1008	0.1628					0.0388	0.1735	0		0.0470			0.0442	0.197	
	b 1	0.0283	0.0321							0.0484		0.0096		0.0686		0.0216	0.0503	0.224	
	b-2	0.0230	0.0298							0.0424		0.0036		0.0694		0.0224	0.0520	0.232	
	b 3	0.0255	0.0320							0.0458		0.0070		0.0670		0.0200	0.0422	0.188	
Average		0.0256	0.0313			0.0030	19.2	−0.0052	−33.3	0.0455		0.0067	43.5	0.0683		0.0213	0.0482	0.215	0.0039
Aqueous hydrochloric acid-phenol extraction	c 1	0.0366	0.0397							0.0500	0.2234	0		0.0466			0.0133	0.193	
	c-2	0.0355	0.0409							0.0497	0.2222	0		0.0456			0.0450	0.201	
	c 3	0.0347	0.0408							0.0478	0.2136	0		0.0490			0.0453	0.202	
Average		0.0356	0.0404	0.1588	0.1802					0.0492	0.2198	0		0.0460			0.0444	0.199	
	d-1	0.0493	0.0554							0.0634		0.0142		[7]0.0672			0.0504	0.225	
	d-2	0.0458	0.0548							0.0629		0.0137		[7]0.0674			0.0509	0.220	
	d-3	0.0498	0.0545							0.0619		0.0127		[7]0.0682			0.0509	0.227	
Average		0.0483	0.0549			0.0127	81.4	0.0145	92.9	0.0627		0.0135	87.7				0.0506	0.226	0.0062
Brewer's grains:																			
Aqueous hydrochloric acid extraction	a 1	0.0025								0.0024	0.0107	0					0.0014	0.006	
	a 2	0.0021								0.0027	0.0122	0					0.0015	0.007	
	a-3	0.0023								0.0013	0.0058	0					0.0008	0.004	
Average		0.0023		0.0103						0.0021	0.0096	0					0.0012	0.006	
	b-1	0.0160								0.0173		0.0152					0.0077	0.034	
	b-2	0.0148								0.0181		0.0160					0.0096	0.043	
	b-3	0.0161								0.0182		0.0161					0.0096	0.043	
Average		0.0156				0.0133	85.2			0.0179		0.0158	102.6				0.0090	0.040	0.0077
Aqueous hydrochloric acid-phenol extraction	c-1	0.0012								0.0018	0.0080	0					0.0010	0.004	
	c 2	0.0010								0.0015	0.0067	0					0.0009	0.004	
	c 3	0.0013								0.0018	0.0080	0					0.0006	0.003	
Average		0.0012		0.0053						0.0017	0.0076	0					0.0008	0.004	
	d-1	0.0162								0.0173		0.0156					0.0093	0.041	
	d-2	0.0158								0.0180		0.0163					0.0094	0.042	
	d-3	0.0160								0.0180		0.0163					0.0100	0.045	
Average		0.0160				0.0148	94.9			0.0178		0.0161	101.5				0.0096	0.043	0.0087
Rice polish:																			
Aqueous hydrochloric acid extraction	a-1	0.0038	0.0036							0.0068	0.0304	0					0.0016	0.007	
	a 2	0.0038	0.0026							0.0082	0.0360	0					0.0029	0.013	
	a 3	0.0035	0.0027							0.0058	0.0259	0					0.0039	0.017	
Average		0.0037	0.0030	0.0165	0.0134					0.0069	0.0309	0					0.0028	0.012	
	b 1	0.0119	0.0076							0.0112		0.0043					0.0062	0.028	
	b 2	0.0110	0.0075							0.0105		0.0035					0.0067	0.030	
	b 3	0.0111	0.0079							0.0113		0.0044					0.0071	0.032	
Average		0.0113	0.0077			0.0076	48.7	0.0047	30.1	0.0110		0.0041	26.6				0.0067	0.030	0.0039
Aqueous hydrochloric acid-phenol extraction	c-1	0.0027	0.0020							0.0077	0.0344	0					0.0096	0.043	
	c 2	0.0017	0.0020							0.0073	0.0326	0					0.0096	0.043	
	c 3	0.0024	0.0020							0.0067	0.0300	0					0.0092	0.041	
Average		0.0023	0.0020	0.0102	0.0089					0.0072	0.0323	0					0.0095	0.042	
	d 1	0.0052	0.0064							0.0141		0.0069					0.0122	0.054	
	d-2	0.0093	0.0082							0.0122		0.0050					0.0118	0.053	
	d 3	0.0138								Lost		Lost					0.0121	0.054	
Average		0.0094	0.0073			0.0071	45.5	0.0053	31.0	0.0131		0.0059	35.3				0.0120	0.054	0.0026

[1] a's and b's digested Saturday morning and filtered Monday morning.
[2] Should have been about 0.0156 gram.
[3] Should have been about 0.0154 gram in b's and d's, none was added in a's and c's.
[4] Should have been about 0.0438 gram.
[5] Should have been 0.0134 gram in b's and 0.0132 gram in d's.
[6] Not included in the average.
[7] Much difficulty in dissolving precipitate in acid-alcohol.
[8] The phosphate-phenol solution was lost before being standardized, but it was approximately the same strength as the phosphate solution.

TABLE 7.

Test of completeness of extraction and influence of phenol in the determination of inorganic phosphorus in plant substances (1913).

(Analyses by A. F. D. Wussow).

SUBSTANCE, METHOD AND DETERMINATION		FIRST EXTRACTION			SECOND EXTRACTION		
		Magnesium pyrophosphate obtained	Inorganic phosphorus	Added phosphorus recovered as magnesium pyrophosphate	Magnesium pyrophosphate obtained	Excess of phosphorus extracted: Magnesium pyrophosphate	Excess of phosphorus extracted: Per cent of sample
		gram	*per cent*	*gram*	*gram*	*gram*	
Gluten feed:							
Aqueous hydrochloric acid extraction	a-1	0.0211	......	......	0.0032	......	......
	a-2	0.0210	......	......	0.0032	......	......
	a 3	0.0209	......	......	......	......	......
Average		0.0210	0.0936	......	0.0032	−0.0003	0
Aqueous hydrochloric acid-phenol extraction	b-1	0.0212	......	......	0.0011	......	......
	b-2	0.0207	......	......	0.0009	......	......
	b-3	0.0200	......	......	0.0011	......	......
Average		0.0206	0.0919	......	0.0010	−0.0024	(?)
Brewer's grains:							
Aqueous hydrochloric acid extraction	a-1	0.0026	......	......	0.0010	......	......
	a-2	0.0028	......	......	0.0010	......	......
	a-3	0.0028	......	......	0.0010	......	......
Average		0.0027	0.0120	......	0.0010	+0.0007	+0.0029
Aqueous hydrochloric acid-phenol extraction	b-1	0.0012	......	......	0.0010	......	......
	b-2	0.0022	......	......	0.0010	......	......
	b 3	0.0026	......	......	0.0010	......	......
Average (2 & 3)		0.0024	0.0107	......	0.0010	+0.0006	+0.0027
Timothy hay:							
Aqueous hydrochloric acid extraction	a-1	0.0064	......	......	0.0012	......	......
	a-2	0.0069	......	......	0.0010	......	......
	a-3	0.0053	......	......	0.0012	......	......
Average		0.0062	0.0276	......	0.0011	+0.0001	......
	a-4	0.0253	......	......	0.0032	......	......
	a-5	0.0250	......	......	0.0033	......	......
	a 6	0.0256	......	......	0.0032	......	......
Average		0.0253	......	[1]0.0191	0.0032	−0.0010	......
Aqueous hydrochloric acid-phenol extraction	b-1	0.0099	......	......	0.0006	......	......
	b-2	0.0099	......	......	0.0005	......	......
	b 3	0.0096	......	......	[2]0.0029	......	......
Average		0.0098	0.0437	......	0.0005	−0.0011	......
	b 4	0.0249	......	......	0.0029	......	......
	b-5	0.0246	......	......	0.0030	......	......
	b-6	0.0252	......	......	[2]0.0006	......	......
Average		0.0249	......	[1]0.0151	0.0029	−0.0012	......
Aqueous hydrochloric acid extraction[3]	a-1	0.0062	......	......	0.0019	......	......
	a-2	0.0040	......	......	0.0016	......	......
	a 3	0.0025	......	......	0.0018	......	......
Average		0.0042	0.0187	......	0.0017	+0.0011	0.0062
Aqueous hydrochloric acid-phenol extraction[2]	b-1	0.0105	......	......	0.0003	......	......
	b-2	0.0097	......	......	0.0006	......	......
	b-3	0.0106	......	......	....	......	......
Average		0.0103	0.0459	......	0.0004	−0.0010	......

[1] Should have been about 0.0153 gram.

[2] Not included in the average.

[3] In the second extraction 200 cc. instead of 250 cc. of the aliquot were used.

TABLE 7—Continued.

SUBSTANCE, METHOD AND DETERMINATION		FIRST EXTRACTION: Magnesium pyrophosphate obtained	FIRST EXTRACTION: Inorganic phosphorus	FIRST EXTRACTION: Added phosphorus recovered as magnesium pyrophosphate	SECOND EXTRACTION: Magnesium pyrophosphate obtained	SECOND EXTRACTION: Excess of phosphorus extracted: Magnesium pyrophosphate	SECOND EXTRACTION: Excess of phosphorus extracted: Per cent of sample
		gram	*per cent*	*gram*	*gram*	*gram*	
Wheat:							
Aqueous hydrochloric acid extraction	a–1	0.0092	......	......	......	....	....
	a–2	0.0096	......	......	......	....	....
	a–3	0.0092	......	......	......	....	....
Average		0.0093	0.0415	......	......	....	....
Aqueous hydrochloric acid-phenol extraction	b–1	0.0040	......	......	......	....	....
	b–2	0.0049	......	......	......	....	....
	b–3	0.0048	......	......	......	....	....
Average		0.0046	0.0205	......	......	....	....
Wheat bran:							
Aqueous hydrochloric acid extraction	a–1	0.0143	......	......	......	....	....
	a–2	0.0134	......	......	......	....	....
	a–3	0.0138	......	......	......	....	....
Average		0.0138	0.0615	......	......	....	....
Aqueous hydrochloric acid-phenol extraction	b–1	0.0145	......	......	......	....	....
	b–2	0.0157	......	......	......	....	....
	b–3	0.0140	......	......	......	....	....
Average		0.0147	0.0655	......	......	....	....
Rice polish:							
Aqueous hydrochloric acid extraction	a–1	0.0186	......	......	0.0026	....	....
	a–2	0.0192	......	......	0.0032	....	....
	a–3	0.0182	......	......	0.0034	....	....
Average		0.0187	......	[4]0.0089	0.0031	0	0
	a–4	0.0098	......	......	0.0012	....	....
	a–5	0.0096	......	......	0.0012	....	....
	a–6	0.0098	......	......	0.0012	....	....
	a–7	0.0098	......	......	0.0012	....	....
Average		0.0098	0.0434	......	0.0012	−0.0004	....
Aqueous hydrochloric acid-phenol extraction	b–1	0.0150	......	......	0.0017	....	....
	b–2	0.0144	......	......	0.0018	....	....
	b–3	0.0150	......	......	......	....	....
Average		0.0148	......	[4]0.0110	0.0017	−0.0008	....
	b–4	0.0036	......	......	......	....	....
	b–5	0.0040	......	......	0.0014	+0.0007	0.0030
	b–6	0.0040	......	......	......	....	....
	b–7	0.0036	......	......	......	....	....
Average		0.0038	0.0169	......	......	....	....

[4] Should have been about 0.0111 gram.

NOTE BY H. S. GRINDLEY AND C. I. NEWLIN.

(1) The methods used were exactly like those outlined in the directions sent out with two exceptions: Dipotassium hydrogen phosphate (K_2HPO_4), was used instead of disodium hydrogen phosphate (Na_2HPO_4); the solutions used were prepared as follows:

Solution A: This is the plain 0.2 per cent aqueous hydrochloric acid which we have been using in our work. The strength of the solution was fixed by titration with standard alkali.

Solution B: Measure carefully into a 1-liter measuring flask 110 cc. of the last standard dipotassium hydrogen phosphate[1] prepared. Also add to the flask 496 cc. of the 2.015 per cent hydrochloric acid in water. Dilute to the mark and shake thoroughly. Transfer to a clean, dry 5 liter bottle or flask and add 4 liters of distilled water. Mix thoroughly and label as follows: "Solution B: 0.2 per cent HCl containing the equivalent of 24.6 mg. of $Mg_2P_2O_7$ per 300 cc."

Solution C: Measure carefully into a 1-liter measuring flask 496 cc. of the 2.015 per cent hydrochloric acid in water and add 250 grams of pure phenol. Dilute to the mark and shake thoroughly. Transfer to a clean, dry 5 liter bottle or flask and add 4 liters of water. Mix thoroughly and label as follows: "Solution C: 0.2 per cent HCl containing 50 grams of phenol per liter."

Solution D: Measure carefully into a 1-liter measuring flask 110 cc. of the standard dipotassium hydrogen phosphate last prepared and also add 496 cc. of the 2.015 per cent hydrochloric acid in water. Now add to this same flask 250 grams of pure phenol. Dilute to the mark and shake thoroughly. Transfer to a clean, dry 5 liter bottle or flask and add 4 liters of water. Mix thoroughly and label the flask containing the solution as follows: "Solution D: 0.2 per cent HCl containing the equivalent of 24.6 grams of $Mg_2P_2O_7$ per 300 cc. and 50 grams of phenol per liter."

(2) The method seems unsatisfactory in that we have been unable to get satisfactory triplicate determinations. Although the triplicate determinations as a rule vary widely we have in all cases taken their average values for a study of the results.

(3) It is evident from the results obtained in these experiments that inorganic phosphates added to feeding stuffs cannot be quantitatively recovered by the method used in this work.

(4) The quantity of the added phosphates recovered is apparently determined by the amount of phytin or other soluble organic-phosphorus compounds present in the feeding stuffs, that is, the smallest percentage was recovered in rice polish which contains the largest quantity of phytin of the four feeds examined. On the other hand, the largest percentage of added phosphate was recovered in the case of the brewer's grains which contain only a trace of phytin or other soluble organic compounds that are precipitated by magnesia mixture in ammoniacal solution.

(5) In our opinion, the incomplete recovery of the added phosphates is due in the main, at least, to the fact that magnesium ammonium phosphate cannot be quantitatively separated from phytin by treatment with 0.2 per cent nitric acid in 95 per cent alcohol.

(6) These conclusions have been undoubtedly confirmed by numerous experiments which we have made to determine the solubility of the magnesium ammonium phosphate and phytin alone and together in mixtures. These later experiments have shown clearly, (a) That magnesium ammonium phosphate, alone, is soluble in 95 per cent alcohol containing 0.2 per cent nitric acid by weight; (b) that commercial phytin, alone, is only slightly soluble in 95 per cent alcohol containing 0.2 per

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[1] The average of 18 determinations of magnesium pyrophosphate in 10 cc. of the standard dipotassium hydrogen phosphate solution equaled 0.03737 gram of magnesium pyrophosphate. The average for each of the six determinations in triplicate were as follows: 0.0374, 0.0369, 0.0370, 0.0372, 0.0375, and 0.0377 gram. The 110 cc. of dipotassium hydrogen phosphate contained phosphorus equivalent to 0.4103 grams of magnesium pyrophosphate. Each 300 cc. of the 5 liters of solutions B and D therefore contained P equivalent to 0.0246 gram of magnesium pyrophosphate.

cent nitric acid; (c) that magnesium ammonium phosphate cannot be quantitatively separated from phytin by treatment with 0.2 per cent nitric acid in 95 per cent alcohol.

DISCUSSION OF RESULTS WITH ANIMAL SUBSTANCES

The neutral molybdate method of Emmett and Grindley, the barium chlorid method of Siegfried and Singewald (provided a sufficient excess of barium chlorid is used), and the magnesia mixture method of Forbes and associates gave satisfactory results, which were practically identical on vacuum-dried muscle.

The barium chlorid method was found inapplicable in the presence of ammonium sulphate, and hence was not useful on extracts of blood and brain prepared with the aid of this reagent.

The neutral molybdate method gave results on blood which were apparently too high, a decomposition of organic phosphorus seeming to result from the heat used during the concentration of the extract. Some difficulty has been experienced in the recovery of inorganic phosphorus added to blood. The recovery has been slightly greater with the magnesia mixture than with the neutral molybdate method.

As compared with the magnesia mixture method, the neutral molybdate method gave, with extract of brain prepared with the aid of ammonium sulphate, higher results for inorganic phosphorus with lower recovery of added phosphates, the differences being slight in two cases and great in one test. The difficulties of filtration are greater with the neutral molybdate than with the magnesia mixture method.

Readily filterable extracts of brain may be prepared by the use of $3\frac{1}{3}$ per cent ammonium sulphate solution in place of 0.1 per cent ammonium sulphate in each place where the latter is specified in the published magnesia mixture method (see p. 219); and the hindering effect of the added amount of ammonium sulphate on the precipitation of phosphorus by magnesia mixture may be overcome by the substitution of 50 cc. of magnesia mixture for 10 cc. as specified, and allowing the precipitates to stand 3 days before filtering. With these modifications the magnesia mixture method is readily workable on brain, concordant results are obtained and added phosphate is all recovered. The work on brain reported in Table 5 was done by this modified method.

In making extracts of brain it is desirable that the analyst be cautioned with reference to the handling of the brain sample during extraction. The coagulum is very soft. It should be stirred only enough to keep it in motion. If once finely broken up it holds onto a great deal of liquid. If roughly handled in returning from the sand filter to the beaker it becomes too much broken up. If the extract is poured onto a thin film of absorb-

ent cotton 1.5 inches in diameter laid over the center of the sand filter the return of the coagulum to the beaker is much facilitated. If the cotton is not broken up by needless stirring it can be taken out of the beaker with a glass rod and returned to the sand each time a partial extract is to be filtered. Care is necessary to prevent loss through bumping, on account of sand in the beakers during the last extractions. Three determinations at a time are enough to handle, but with some risk of loss one can handle six. Each partial extract should be boiling-hot at the time filtration begins.

In the trial reported on page 229 all the phosphate was recovered except 0.0009 gram of magnesium pyrophosphate. In the trial reported in Table 5 the loss was 0.0004 gram of magnesium pyrophosphate.

The neutral molybdate method can not be used satisfactorily with extracts prepared as suggested above, and it is not practicable to prepare cold water extracts of brain as specified in the neutral molybdate method.

The test of the influence of heat on inorganic phosphorus estimation in blood, as set forth in Table 4, shows that the high results on blood obtained by the neutral molybdate method must be due to the cleavage of organic phosphorus by the heat used in the evaporation of the extract. While the duration of heating used in this method is much greater than in the preparation of hot-water ammonium sulphate extracts of tissues as in the magnesia mixture method, this test raises the question of the existence and magnitude of such cleavage. This should be investigated especially with reference to tissues containing phosphocarnic acid, which is said to be rather easily decomposed by heat.

The recovery of added phosphates from the extract of muscle by the magnesia mixture method has usually been practically complete (see Table 1). In the last analyses of Wussow (Table 3), however, the recovery of added phosphate was appreciably incomplete, though the determination without the added phosphate was higher than by the neutral molybdate method, where the recovery of added phosphate was practically complete. The low recovery of added phosphate from both blood and muscle, as reported in this table, suggests that the conditions were not perfect for the precipitation of this amount of magnesium ammonium phosphate. With brain the recovery of added phosphate was complete, since special measures were taken to insure complete precipitation. The same measures, namely, increased amount of magnesia mixture and increased time for precipitation should be tried out on these other tissues.

The magnesia mixture method has usually given satisfactory results on all the animal substances with which it has been used. Further work on this method is needed, however, on the influence of the heat used in the preparation of the extracts, and the matter of preparation of blood samples for analysis should also receive attention.

DISCUSSION OF RESULTS WITH PLANT SUBSTANCES.

The test of Collison's method (see Table 2) showed that this procedure was much more easily workable than the Forbes method, and the recovery of added phosphates was commonly more nearly complete, but unfortunately the extraction was shown not to be complete, or else the reagent causes cleavage of organic phosphorus compounds, since the second and even the third extraction yield significant amounts of inorganic phosphorus (see notes of Grindley and Ross, p. 225, and analyses of Wussow, Table 2). This method therefore seems to be without promise.

The acid-alcohol method of Forbes and associates as published in Ohio Bulletin 215 and as outlined for these coöperative tests on pages 231 to 232 of this report commonly yields extracts which are difficult to filter. The centrifuge should be used to facilitate filtration.

Enzymatic cleavage apparently affects results during protracted filtration, as made evident by the fact that the more prolonged the filtration the higher the result. The addition of phenol, however, seems to prevent this cleavage, and phenol as used in this work was shown by quantitative tests not to hinder the precipitation of magnesium ammonium phosphate.

This method should be distinguished from the magnesia mixture method of Forbes and associates for animal products. The plant method is based on the acid-alcohol separation of phytin and inorganic phosphates, and as this was called the "acid-alcohol method" in our original publication it is proposed that this name be retained.

In Tables 6 and 7 it may be seen that the presence of phenol gave lower results for inorganic phosphorus with alfalfa, brewer's grains, rich polish, gluten feed, and wheat, and higher results with blue grass, timothy hay, and wheat bran. The recovery of added phosphorus was usually incomplete and higher with phenol than without. It was complete with some of the tests with brewer's grains, timothy hay, and rice polish.

Since phenol has been found to be without effect on the precipitation of magnesium ammonium phosphate, the marked results attending its presence in inorganic phosphorus estimations may be due to its effect on enzyms. Since this effect is usually in the direction of lower results, though sometimes higher, it is to be supposed that in the former cases cleavage predominated except as suppressed by phenol, while in the latter cases the inhibited processes were in the direction of synthesis. That such a state of affairs is not impossible is indicated by the work of Harden, Young, Norris, Von Lebedev, and Euler and associates on the synthesizing enzyms of yeasts and molds. The indications are that the use of phenol in this method is desirable.

Grindley and Newlin state (p. 235) that magnesium ammonium phosphate can not be separated from commercial phytin by treatment with 0.2 per cent nitric acid in 95 per cent alcohol, and they explain the difficulty in recovering added phosphate as "determined by the amount of phytin or other soluble organic-phosphorus compounds present in the feeding stuffs." They cite the minimum recovery of added phosphates from rice polish and also its maximum phytin content. Wussow, however, obtained a complete recovery of added phosphate from rice polish in one case but only one-third to one-half of the same in other work.

It has been previously shown that magnesium ammonium phosphate can be separated from that member of the phytin group contained in wheat middlings (Ohio Agr. Exper. Sta. Bul. 215, p. 475), and also that magnesium ammonium phosphate can be recovered from the extract of alfalfa, though in this series of determinations the amounts of alfalfa extract were less than in an inorganic phosphorus estimation (ibid., p. 472). In later work, however, in our own laboratory and elsewhere, added phosphate has not been completely recovered from alfalfa extracts.

At least a part of the incompleteness of recovery of added phosphates is due to the mechanical character of the precipitates, notably so in the case of alfalfa. That the phosphate is mechanically held by the gelatinous precipitate is shown to be probable by the results with alfalfa in Table 6. In the work reported by Trowbridge and Smith the precipitate remained an extra day in acid-alcohol and the recovery of added phosphate was more nearly complete, both with and without phenol, than in the work by Wussow. So far as this incompleteness of recovery of added phosphates is due to the mechanical character of the dried precipitate it can probably be overcome by the employment of such mechanical means as may be necessary to reduce it to a finely-divided condition, as, for instance, shaking with glass beads.

A test of the completeness of extraction of inorganic phosphates by 0.2 per cent hydrochloric acid in 3 hours was made with gluten feed, brewer's grains, timothy hay, and rice polish, the results being given in Table 7.

In considering the significance of the weight of pyrophosphate obtained from the second extraction one should bear in mind the fact that this is due largely to dissolved phosphate from the first extraction remaining adherent to the foodstuffs. After making the necessary correction of this weight by subtracting such amount of magnesium pyrophosphate as corresponds to the inorganic phosphorus in the liquid retained by the sample, the results are very small, and are more often minus quantities than not; showing that with these four foodstuffs the 3-hour extraction is as nearly complete as our methods allow us to measure. Work with larger precipitates would settle the point more satisfactorily.

REPORT ON HEAVY METALS IN FOODS.

By H. M. Loomis, *Associate Referee.*

The work on the subject of heavy metals this year included arsenic, lead, and tin, these metals seeming to require the most attention at the present time. The study of the determination of any one of these metals constitutes a large subject in itself, and the associate referee would not have been able to undertake the work on all three of them without the special assistance of E. L. P. Treuthardt, of the Bureau of Chemistry, who took charge of the work on tin and whose report is presented as a separate paper. E. O. Eaton and C. R. Smith, of the Bureau of Chemistry, were also of great assistance by doing preliminary work and offering suggestions on arsenic and lead determinations.

ARSENIC.

Samples and instructions for the arsenic work were sent out to thirteen collaborating chemists, nine of whom sent in reports. After careful consideration and consultation, it was decided to limit the work to the following modifications of the Gutzeit method:

MODIFICATION OF SANGER-BLACK METHOD (C. R. SMITH, BUR. CHEM. CIR. 102).

(*a*) *Destruction of organic matter by digestion.*—Weigh out 25 grams of sample, transfer to a 500 cc. round-bottom flask and digest with 10 cc. of concentrated sulphuric acid and 10 cc. of concentrated nitric acid. Both acids should be arsenic-free. Heat until the mixture turns dark brown or black, then add more nitric acid in 10 cc. portions, heating between each addition until the liquid remains colorless or yellow, even after evolution of SO_3 fumes. To remove completely all nitric or nitrous acids, evaporate to about 5 cc., and if on addition of water to the cooled acid, nitrogen peroxid fumes are evolved, a second evaporation to white fumes is necessary.

Reduction of arsenate to arsenite.—Dilute the acid solution to 25 cc. and add 0.75 gram of potassium iodid; heat to about 90°C., add several drops of dilute stannous chlorid (about 5 per cent) to reduce all iodin liberated and continue the heating for 10 minutes. Cool and make up to 100 cc. with 1 to 4 sulphuric acid; introduce 20 cc. portions of this solution into the 2-ounce generator bottle, add 20 cc. of 1 to 4 sulphuric acid and 3 or 4 drops of 40 per cent stannous chlorid solution to sensitize the zinc, connect up the generator and run as in the preparation of standards. Run a blank test with the reagents alone.

(*b*) *Separation from organic matter by precipitation with magnesium-phosphate mixture.*—In the case of the sweetened gelatin, heat 25 grams with 25 cc. of 10 per cent hydrochloric acid in a covered beaker for 1 hour on a steam bath, add 20 cc. of bromin water, neutralize with ammonium hydroxid, add 2 grams of arsenic-free di-sodium hydrogen phosphate and precipitate with an excess of magnesia mixture. Wash the precipitate with 2½ per cent ammonia, drain and dissolve off into the generator bottle with 1 to 4 sulphuric acid, using about 40 cc. for dissolving the precipitate and washing the filter. Add 3 or 4 drops of 40 per cent stannous chlorid and proceed as in the preparation of standards.

In the case of the fruit sirup, weigh out 25 grams and add bromin water in slight excess, neutralize with ammonium hydroxid, precipitate by addition of sodium phosphate and magnesia mixture, and proceed as in the case of jelly.

Preparation of standards.—Follow the method given under "Standards" in Bureau of Chemistry Circular 102, using the 2-ounce generator bottles, 1 to 4 sulphuric acid and 15 grams of stick zinc, if possible. If other apparatus or reagents are used, please so indicate in your report.

In the case of "heavy" arsenics—50 to 60 micromilligrams—have the generator bottle only half full so as to dilute the arsin, otherwise it may come off in such a concentrated form as to give a dull black colored strip, instead of deep orange. (This does not usually happen except with standards.)

OTHER MODIFICATIONS OF GUTZEIT METHOD FOUND SATISFACTORY.

The samples prepared for analysis were, first, a sweetened gelatin solution, prepared from arsenic-free gelatin and sugar, to which sodium arsenite in the proportion of 7 mg. of arsenic trioxid (As_2O_3) per kilo was added; second, a fruit sirup prepared in the laboratory to which sodium arsenite in the proportion of 4 mg. of arsenic trioxid (As_2O_3) per kilo had been added.

The following results were reported:

RESULTS OF COÖPERATIVE WORK.

Arsenic in sweet jelly and fruit sirup.

ANALYST	ARSENIC IN SWEET JELLY			ARSENIC IN FRUIT SIRUP		
	Smith modification		Other laboratory methods	Smith modification		Other laboratory methods
	Digestion	Precipitation		Digestion	Precipitation	
Courtney Conover	6.0	...	8.0	4.0	...	4.0
W. S. Allen	7.0	...	10.0	4.0	...	4.0
E. H. Berry	5.0	4.6	4.6 4.6	4.0	4.0	4.0
W. W. Karnan	7.6	8.0	...	3.2	3.6	...
E. O. Eaton	5.0 6.0 6.0	...	...	6.0 6.0 8.0	...	...
T. F. Pappe	6.6	6.6	...	4.0	4.5	...
H. D. Poore	...	7.2 7.0 6.3 7.2	...	...	4.9 5.0 5.3 5.1	...
C. R. Smith	6.0 6.5 6.5	6.5 7.0	...	4.5	4.5 5.0 4.6	...
H. E. Woodward	6.0	5.0	...	5.0	4.0	...
Maximum	7.6	8.0	...	8.0	5.3	...
Minimum	5.0	4.6	...	3.2	3.6	...
Variation	2.6	3.3	...	4.8	1.7	...
Average	6.2	6.5	...	4.9	4.6	...

COMMENTS OF ANALYSTS.

Courtney Conover: There is possible danger in using glass digestion flasks containing arsenic, and advantage in using porcelain casseroles for digestion. I recommend 4 cc. of 20 per cent potassium iodid solution for the reduction of the

arsenic, 8 grams of zinc and mercuric chlorid test paper instead of paper prepared with mercuric iodid. In order to expel the nitrous fumes I diluted the digestion and boiled down several times.

W. S. Allen: (Method of Circular 102): I have found that the preliminary precipitation as magnesium arsenate was unsatisfactory, since I can not recover over 70 per cent of the arsenic in preliminary experiments. In preparing standard stains and making all determinations with the 5 per cent mercuric bromid paper, it was noted that the color strip on one side was considerably longer than on the other side. In some cases this amounted to a difference of ½ inch in a maximum length of ¾ inch. It was not possible to make very accurate readings, as small differences in the amount of arsenic make very little difference in the length of stain. The use of potassium iodid was omitted, as I have found from my own investigations that stannous chlorid will easily and completely reduce arsenates. It was found difficult to remove all iodin when following the potassium iodid reduction procedure. Even after adding a few drops of stannous chlorid to reduce the iodin liberated, and no color of iodin was apparent, violet vapors of iodin would be given off in the Gutzeit apparatus, producing a stain somewhat similar to that given off by arsenic. I substituted, therefore, for the potassium iodid 0.5 cc. of 80 per cent stannous chlorid solution, which I believe is preferable to potassium iodid as a reducing agent. Instead of stick zinc I used 15 grams of Baker and Adamson shot zinc in preparing standards and running analyses.

General Chemical Company method: Samples were prepared by oxidation with the nitric and sulphuric acid mixture, as in above method. The arsenic was then determined on aliquots of this oxidized solution by the method of Allen and Palmer (*Proceedings of the Eighth International Congress of Applied Chemistry*, vol. 1, p. 9). No trouble is found in obtaining color stains of the same length on each side of the paper. Moreover, the reading differences between different standard stains, when using a 0.5 per cent mercuric chlorid solution, are so much greater than with a 5 per cent mercuric bromid that it is possible to read with much greater accuracy.

E. H. Berry: The preliminary precipitation method works very well and seems preferable to one which requires the use of potassium iodid. It is almost impossible to avoid the precipitation of stannous iodid even when using acid weaker than 1 to 5. In fact, it does not seem necessary to use potassium iodid as a reducing agent, as determinations made without its use checked very closely with those in which it had been used. In the case of gelatins it would seem that the decomposition with acids can be eliminated. Dissolve the gelatin in 1 to 4 sulphuric acid, boil until the solution begins to blacken, then dilute to the original volume and introduce this solution into the generator bottles. It is scarcely necessary to use 15 grams of zinc, half that amount being sufficient.

W. W. Karnan: In all cases the hydriodic acid reduction was made on the aliquots preparatory to introduction into the generator bottle. Also sodium ammonium phosphate was used instead of disodium hydrogen phosphate in the precipitation method. The magnesium phosphate precipitation method seems to be very effective and convenient on substances which are in solution or which dissolve easily in dilute acid, and is much to be preferred to the acid digestion method whenever it can be conveniently used. It has been my experience in this work that to be certain of getting complete evolution of arsenic as arsin, it is invariably necessary to make the preliminary reduction before making the final run. In this reduction, in order to prevent the precipitation of stannous iodid (which seems very prone to occur) I kept the acid solution even weaker than 1 to 5, if possible, was careful to add no more stannous chlorid than was necessary during the heating, and kept the potassium iodid down to between 0.5 and 0.75 gram (added as 50 per cent solution).

E. O. Eaton: I found Smith's modification very hard to work for duplicate aliquot determinations. The trouble seemed to be in the rate of flow of the generated gases. Several were run in a bath at 15°C., but the bands were not uniform. I believe it would be advisable to add an inhibiting substance to get a minimum flow of gas, and let it run for a much longer time. On some of the strips the arsenic-mercury complex did not seem to be saturating the paper, but spread too rapidly. This could not be controlled. I think it happens only on pure substances, such as gelatin, by the digestion method where there are very few salts present.

H. D. Poore: I find that 1 to 4 sulphuric acid used for dissolving the precipitate of magnesium ammonium arsenite is too strong because action with the zinc in generating the arsin is not rapid enough; 1 to 8 acid works much better. I favor 1 to 4 hydrochloric acid rather than sulphuric acid, as it gives better action with no possibility of hydrogen sulphid being formed. I have also obtained in my previous work with arsenic the same results when adding to the generating bottle the potassium iodid and stannous chlorid and generating at once with the zinc, heating later instead of heating at first and then cooling before adding the zinc. Although I obtained lower results with the digestion method, I did not run another determination, believing that either loss of arsenic takes place or that the arsenate is not readily reduced to arsenite, due perhaps to retained nitric acid.

C. R. Smith: I would like to state that I think the hydriodic acid reduction is best performed on the aliquot just before the generation because the hydriodic acid is oxidized by the air, giving free iodin on long standing, which in turn oxidizes the arsenic. I expect some will have trouble with the hydriodic acid reduction because the sulphuric acid should not be stronger than 1 to 4 (preferably between 1 to 4 and 1 to 5); if it is stronger a precipitate of stannous iodid may be formed and also a large amount of hydrogen sulphid.

H. E. Woodward: I found much trouble in using the strength of acid recommended, and had to cut it down considerably in order to prevent too rapid evolution of gas; using a diluted solution and adding potassium sulphate I was able to get very satisfactory deposits. I also used 1 gram of potassium sulphate in a generator with 10 cc. of 10 per cent sulphuric acid in making the standard stain.

DISCUSSION.

The results with the Smith method appear to be very good and it seems necessary to do only a little more work to clear up certain minor difficulties experienced by the analysts. Special difficulty seems to be found with the use of potassium iodid and the proper strength and nature of the acid to be used in the generator. Mr. Smith's comment regarding the reduction with hydriodic acid appears very important and also Mr. Conover's warning regarding the presence of arsenic in certain glassware. On the whole the precipitation method with magnesium phosphate appears to be the most satisfactory and convenient where it can be applied; that is, to materials in complete solution, or which can readily be dissolved, and which do not themselves cause an organic precipitate with magnesia mixture in alkaline solution. The method of Allen and Palmer appears to warrant study by the association.

LEAD.

The work on lead this year was confined to its determination in baking powder and baking powder chemicals. After a study of the literature on the subject and some experimental work, the following methods were taken up for collaborative study: (1) Seeker and Clayton gravimetric method for alum-phosphate baking powders; (2) Potter's modification of the Teed method; and (3) the Teed method modified by the use of sodium bisulphite.

The samples sent out for analysis consisted of, first, a lead-free alum phosphate solution, containing hydrolyzed starch, to which 1.8 mg. of lead per 100 cc. were added; second, a lead-free sodium tartrate solution containing hydrolyzed starch, to which 1.2 mg. of lead per 100 cc. were added.

SEEKER AND CLAYTON GRAVIMETRIC METHOD.

In the method as sent out by the referee 20 cc. of 10 per cent hydrochloric acid were recommended instead of 10 cc.; this change seemed to be an improvement, as it reduced the precipitate thrown down on passing in hydrogen sulphid to an amount easily handled, whereas with 10 cc. acid the precipitate was very bulky. Mr. Seeker has written that he still believes 10 cc. of acid are preferable and several of the analysts reported results on the original method.

POTTER'S MODIFICATION OF TEED METHOD.

Preparation of standards.—Dissolve 200 grams of tartaric acid, 44 grams of ammonium chlorid, and 44 grams of potassium chlorid in 500 cc. of water and render alkaline to litmus with ammonium hydroxid. Add 20 cc. excess and 10 cc. of fresh colorless ammonium sulphid solution (2 cc. of concentrated ammonium hydroxid diluted to 10 cc. and saturated with hydrogen sulphid). After letting stand overnight filter through asbestos and boil until escaping vapor does not darken lead acetate paper. Filter the now acid solution through asbestos, treat with 5 grams of hydrazin sulphate, or the equivalent amount of hydrazin hydrochlorid, 40 cc. of concentrated hydrochloric acid, and 200 cc. of 8 per cent gum arabic solution. Boil 2 minutes after any bitartrate which may have formed is dissolved, cool somewhat, add 5 cc. of 10 per cent potassium cyanid and make just ammoniacal to litmus. Add exactly 20 cc excess of ammonium hydroxid and dilute to 1200 cc. For each standard mix 60 cc. of this solution, which should be colorless and slightly opalescent, with the desired amount of standard lead nitrate solution (concentrated if necessary) and treat with 1 cc. of fresh colorless ammonium sulphid solution. Dilute to 100 cc. The standards should contain 0.1 0.3, 0.6, 0.9, 1.2, and 1 5 mg. of lead. To prepare the standard lead nitrate solution, pulverize some crystals and dry the powder over sulphuric acid. Dissolve 0.8 gram in 500 cc. of water and a few drops of nitric acid in a graduated flask. Dilute 20 cc. of this solution to 1 liter. Each cubic centimeter contains 0.02 mg. of lead.

Determination.—To a 50 cc. sample of tartrate solution add 20 cc. of saturated hydrazin sulphate (about 0.4 gram of the salt) and boil 2 minutes. If the yellow color does not disappear, add a little solid hydrazin salt and boil again, but only for a moment. Any remaining color is due to organic matter. Remove from the flame, add 10 cc. of 8 per cent gum arabic solution and bring to boiling. Cool, add 1 cc. of 10 per cent potassium cyanid and neutralize closely with concentrated ammonium

hydroxid using a burette and litmus paper. Add exactly 1 cc. excess and exactly 1 cc. of fresh colorless ammonium sulphid solution. Dilute to 100 cc., mix well and stopper in a graduated tube. Prepare one new standard containing 0.6 mg. of lead. After 24 hours correct the old standard of the same concentration against the new by comparison in a colorimeter. Correct the other members of the series from the corrected value, that is, read 0.6 against 0.9, 0.9 against 1.2, etc. Read the solution of the sample against the nearest color in the series.

If starch is present, dissolve the sample in 160 cc. of 1 to 7 hydrochloric acid at zero and filter at once through asbestos. Concentrate the clear solution on a water bath to 50 cc. and analyze as just described, beginning after the filtration with the following exception: Read at once against a new standard to which 5.2 grams of lead-free ammonium chlorid have been added. If any starch has dissolved, a yellow color will result before adding ammonium sulphid. This can be approximately corrected by reading before and after adding the sulphid against the standard.

SODIUM BISULPHITE MODIFICATION OF TEED METHOD.

Add to 50 cc. of solution (equal to 10 grams of baking powder) 2 cc. of sodium bisulphite solution,[1] heat to incipient boiling, and test a few drops of the solution with potassium sulpho-cyanid reagent to see if all the iron is reduced to the ferrous state; if not, repeat the treatment with bisulphite solution. Cool, add 1 cc. of 10 per cent potassium cyanid solution and strong ammonia till just neutral to litmus, then 1 cc. in excess. Boil gently until clear and colorless, cool, and make to 100 cc. Add 2 drops of freshly-prepared colorless ammonium sulphid solution, mix well, and compare with standards prepared as follows:

Dissolve 1.6 grams of crystallized lead nitrate, dried over sulphuric acid, in a liter of water containing a few drops of dilute nitric acid; each cubic centimeter of this solution equals 1 mg. of lead. This solution should be diluted 100 times for use in making up the color standards.

Lead-free tartrate solution for use in making up the standards may be made as follows:

Dissolve 200 grams of tartaric acid in about 500 cc. of hot water, cool, add 40 cc. of sodium bisulphite solution, heat to incipient boiling and test for complete reduction of iron with sulphocyanid as above, cool, then add 20 cc. of 10 per cent potassium cyanid and concentrated ammonia till the solution is distinctly alkaline to litmus paper. Boil until the solution clears, cool, add 2 cc. of freshly-prepared colorless ammonium sulphid, dilute to 1 liter, and allow to stand overnight in a tall cylinder. In the morning the lead sulphid will be found to have settled and can be removed by filtration. Boil the filtrate to remove hydrogen sulphid, cool and dilute to the original volume. To 50 cc. of this solution are added desired amounts of the standard lead solution. Dilute to 100 cc. and add 2 drops of colorless ammonium sulphid to make the standards. Mix well and compare with the solution of the sample, similarly treated, in a colorimeter.

The sample should finally be compared with a standard, containing approximately the same amount of lead, in order to get correct results, and the addition of ammonium sulphid solution should be made to the standards and the sample solution at the same time, as the colors will change on standing.

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[1] This bisulphite solution may conveniently be prepared by passing sulphur dioxid gas into a 10 per cent solution of anhydrous sodium carbonate until the evolution of carbon dioxid ceases. Dilute a little of this solution, as needed, with 10 parts of water for use as the above reagent.

Samples and instructions were sent out to eleven collaborators, eight of whom have sent in reports as follows:

RESULTS OF COÖPERATIVE WORK.

Lead in phosphate and tartrate solutions.

LEAD IN PHOSPHATE SOLUTION			LEAD IN TARTRATE SOLUTION		
Analyst	Original Seeker-Clayton method	Seeker-Clayton method using 20 cc. instead of 10 cc. of 10 per cent hydrochloric acid	Potter method	Bisulphite modification of Teed method	Allen modification of Teed method
	mg. per 100 cc.	*mg. per 100 cc.*	*mg. per 100 cc.*	*mg. per 100 cc.*	*mg. per 100 cc.*
Courtney Conover	...	1.5 2.0	....	....	...
E. H. Berry	...	1.6 1.79	1.45	1.43	...
P. B. Dunbar	3.4	1.4	1.2	1.3	1.2
E. O. Eaton	...	0.84 0.84	1.4 1.4	1.2 1.3	...
W. W. Karnan	...	...	1.4	1.6	...
T. F. Pappe	(1)	...	1.4	...	1.0
A. F. Seeker	2.1	...	1.2	(2)	...
H. E. Woodward	(1)	...	1.11 1.01 0.96 1.23	1.5 1.4 1.35 1.26	...
C. R. Smith	1.73	...	1.40	1.6	...
Maximum	....	...	1.45	1.6	...
Minimum	....	...	0.96	1.2	...
Variation	....	...	0.49	0.4	...
Average	....	...	1.26	1.3	...

[1] No sample sent.

[2] Determination lost.

COMMENTS OF ANALYSTS.

E. H. Berry: There seems to be little choice between the two colorimeter methods. The use of gum arabic in the Potter modification makes it possible to keep the two standards for some time, which is an advantage. The gum causes a slight turbidity, however, making it difficult to get a good comparison. This more than offsets the the advantage gained by the use of the gum. The gravimetric method, although long and tedious, works very well. The fact that the lead is precipitated and weighed makes the method an excellent one for use in court cases. While it appears to have been recommended especially for phosphate products, it might be well to use it on tartrate solutions for checking results by color comparison.

P. B. Dunbar: The bisulphite modification of the Teed method seems to work very satisfactorily. The use of sodium bisulphite appears to have a decided advantage over sodium thiosulphate, as no separation of sulphur occurs. The Potter modification appears to have no advantage whatever over the bisulphite modification. It is much longer and more complicated, and the introduction of reagents after the removal of lead may possibly result in the reintroduction of lead. The directions for making lead-free standard solution are not satisfactory. It is possible to dissolve 200 grams of tartaric acid and 44 grams of ammonium chlorid in 500 cc. of water, but on addition of potassium chlorid a precipitate appears. By increasing the dilution to about 800 cc. and keeping the temperature near boiling, a clear solu-

tion may be maintained until the addition of hydrochloric acid, when a heavy precipitate of bitartrate appears, which can not be dissolved by boiling. If the subsequent treatment is carried out without paying any attention to this precipitate, it finally dissolves on the addition of ammonia.

Since making determinations by the Seeker-Clayton method, I have had some correspondence with Mr. Seeker regarding some of the difficulties encountered. Following his suggestions I have obtained some 10 cc. crucibles and have also digested the sulphuric acid mixture to dissolve basic sulphate of iron, which may be present at that stage. With these changes I have made determinations on samples of calcium phosphate and alum containing amounts of lead varying from 30 to several hundred parts per kilogram. The duplicate results obtained have agreed very well, and have checked other analysts satisfactorily, so that I believe with a little practice in the use of the method, concordant results can be obtained.

E. O. Eaton: I do not see how the Potter method can be satisfactory, as it takes for granted that the lead is present as a salt soluble in hydrochloric acid. It may be present as an insoluble salt, or as metallic lead, and would not be found by this method. Further, the method of eliminating starch is not satisfactory, and if present interferes with the final reading. The use of sodium bisulphite in the other modification of the Teed method is a great advantage, inasmuch as you do not get any free sulphur, which eliminates long boiling and the liability of forming lead sulphid. The presence of inverted starch products does not seem to influence materially the solution for colorimetric assay. The dextrinized products also have a tendency to hold the lead sulphid in colloidal suspension, and can be read many hours after standing. The standards, if not read at once, should contain an added amount of inverted starch or dextrin.

The Seeker-Clayton method appears to be satisfactory with the proper precautions. I found it necessary to have the solution very acid in order to hold the salts in solution for the precipitation with hydrogen sulphid. It was not necessary to let the precipitated sulphid stand over an hour before filtration. Great care should be taken in packing the Gooch crucibles for the final weighing.

C. R. Smith: While I have had experience with determining lead colorimetrically, I have of late determined it gravimetrically in both tartrate and phosphate solutions in preference.

H. E. Woodward: It was rather difficult to compare the unknown with the standards in the colorimetric methods because of a difference in color, due perhaps to the fact that the unknown was made with starch and sodium carbonate in addition to tartaric acid. The Dubosc colorimeter was used. When a large number of samples must be examined for lead, the Potter method is advantageous because the colors do not have to be compared immediately after adding ammonium sulphid, and because the standards keep so long, but for ordinary work I prefer the other method as it is easier, and also because I have always had better results by it. Sodium bisulphite as a reducer is an improvement over sodium thiosulphate in that the latter often gives a turbid solution.

W. W. Karnan: The Seeker-Clayton method I have found very satisfactory, especially where the amount of lead is comparatively high. Where the amount of lead is small and the actual weight of lead chromate obtained is about 1 mg. (which is not infrequent on a small sample), it seems to me that a more accurate measurement of the lead can be had by treating the ammonium acetate solution of the lead sulphate precipitate according to the Teed or Potter colorimetric methods. There seems to be some danger of loss by incomplete solution of the lead sulphate in the ammonium acetate. In the determination mentioned, where the lead content was

10 mg., I found it necessary to warm the mixture to insure complete solution, which may possibly account for the low result in the 2.5 mg. sample.

The Teed method seems to be simpler than the Potter method, both in making the determination and in the preparation of the lead-free tartrate solution, but this is no doubt offset by the fact that the standards in the Potter method are fairly permanent, while those in the Teed method precipitate overnight. The permanency of Potter's standards, however, seems to be only relative. I found that after three or four weeks, with occasional readdition of ammonium sulphid, they finally became unsatisfactory, due, apparently, to the fact that they had commenced to fade unevenly. It may be, however, that a little more care in preparing and keeping will obviate this. Teed's standards and color solutions change so rapidly, that care had to be taken to mix them thoroughly before and after adding the sulphid reagent, otherwise development of color was not uniform. I also noticed, especially with Potter's method, what is apt to be a general fault with colorimetric methods, namely, that the tint of the unknowns would be different from the standards. This was noticeable, for example, in the above determination on cream of tartar baking powder by the Potter method. The unknowns possessed a decided reddish tint which by direct comparison read 0.6 to 0.7 mg., while by the colorimeter (Schreiner) read 0.53 mg., the actual lead content being 0.5 mg. It would appear, however, that these methods should work very satisfactorily in experienced hands.

Experiments were also made on two commercial baking powders, one a cream of tartar powder and the other an alum powder, to which known amounts of lead had been added in the form of lead nitrate solution.

In the case of the tartrate, a blank was run on 20 grams, the final solution being made up to 100 cc., and 50 cc. portions tested by both the Teed and Potter methods. To each of two 20-gram portions of the powder 2.5 mg. of lead were added in the form of lead nitrate solution, and run through the procedure. The final volume of solution in each case was 100 cc., 20 cc. aliquots (equivalent to 0.5 mg. of lead) being taken for the reading. Samples were dissolved in 25 cc. of distilled water and 25 cc. of 1 to 3 hydrochloric acid in the cold, diluted to approximately 150 cc., and filtered through washed asbestos in a Gooch crucible. Iodin test for starch was made on all filtrates with negative results. After concentration on the steam bath, solutions were made up to 100 cc. with distilled water and aliquots taken for the respective determinations as stated above.

In the case of the alum powder, the lead was run by the Seeker and Clayton method except as noted below. A blank was run separately on 20 grams. Two separate portions of 10 grams each were also taken, to which were added respectively 2.5 mg. and 10 mg. of lead in the form of lead nitrate solution. In the 10 mg. sample, just previous to the chromate precipitation, the solution was made up to 100 cc., and only 60 cc. (equivalent to 6 mg. of lead) were used for the gravimetric determination. The remainder was used for a colorimetric determination by simply neutralizing a suitable aliquot with concentrated ammonia, adding 1 cc. in excess, transferring to a 100 cc. Nessler tube, together with 50 cc. of the lead-free tartrate solution, making to volume, and comparing with standards as usual.

Results obtained on the cream of tartar baking powder.

Teed—Blank on 10 grams powder—0.0 mg. of lead.
Potter—Blank on 10 grams powder—0.0 mg. of lead.

Method	*Mg. of lead added*	*Mg. of lead found*
Teed	A 0.5 (×5)	0.50 (×5)
	B 0.5 (×5)	0.51 (×5)
Potter	A 0.5 (×5)	[1]0.53 (×5) (reddish tint) by colorimeter.
	B 0.5 (×5)	[1]0.53 (×5) (reddish tint) by colorimeter.

[1] Direct readings gave approximately 0.6 to 0.7 mg.

Results obtained on the alum baking powder.

Blank on 10 grams powder............................0.26 mg. of lead.

Method	*Mg. of lead added*	*Mg. of lead found*
Seeker and Clayton	A 2.5	2.37 − 0.26 = 2.11
	B 6.0	5.76 − 0.26 = 5.50
Seeker and Clayton combined with Teed	A 0.5	0.5

DISCUSSION.

The results by the two colorimetric methods with tartrate solution are very satisfactory. As the sample sent out, however, consisted of a tartrate solution, it seems best to do further work on these methods next year, using samples of baking powder. To make the bisulphite modification of the Teed method applicable to baking powder, I would suggest the following preliminary directions for preparing the baking powder solution.

PRELIMINARY PROCEDURE FOR PREPARING BAKING POWDER SOLUTION.

Weigh out 20 grams of baking powder, well mixed, into a 250 cc. casserole, add water a little at a time with stirring until reaction is completed. Then add hydrochloric acid (1 : 1) in the same way until the excess of carbonate is decomposed. Add 5 cc. of acid in excess, cover with a watch glass and digest on a steam bath until a test with iodin solution shows the absence of starch. Filter through a fluted filter, and wash the filter several times with small portions of hot water. If lead particles are visible on the filter, or the presence of lead in the metallic state is suspected, treat any residue on the filter with several small portions of hot nitric acid (specific gravity 1.2), collect the acid solution in a separate small porcelain dish, evaporate this solution to dryness on a water bath and expel nitric acid by several treatments and evaporations with a few drops of concentrated hydrochloric acid. Rinse the contents of the dish through a small filter into the main solution and make up to 100 cc.

PRELIMINARY PROCEDURE FOR TARTARIC ACID OR CREAM OF TARTAR.

Weigh out 10 grams of the well-mixed powdered sample, dissolve in 50 cc. of hot water, using also 5 cc. of 1 to 1 hydrochloric acid, filter, and treat filter with dilute nitric acid, and proceed as directed for baking powder. Where lead is present in the metallic state and is, therefore, very unevenly distributed through the sample, it is better when possible to use a larger sample, say 100 grams, making the solution up to the corresponding volume, before taking portions for the colorimetric determination.

The Seeker and Clayton method has a distinct advantage for forensic work, as it allows the separation and identification of a lead compound

and its presentation as evidence. The coöperative work on this method, however, was unsatisfactory and hardly sufficient to judge fairly its merits. It appears to give satisfactory results in the hands of experienced analysts.

TIN.

See supplementary report by E. L. P. Treuthardt.

RECOMMENDATIONS.

It is recommended—

(1) That the methods for the determination of lead in baking powder and baking powder materials, which were studied this year, be made the subject of further study.

(2) That the methods for the determination of arsenic, substantially as given in Bureau of Chemistry Circular 102 and in the *Proceedings of the Eighth International Congress of Applied Chemistry*, volume 1, page 9, be studied for another year.

(3) That the procedure of digesting the sample by the use of nitric and sulphuric acids in the determination of tin be further studied. In this connection it is desirable to develop further procedures applicable to meats and fish in which the time required may be shortened and which will allow the use of a larger sample.

(4) That the gravimetric method for tin, including modifications using Gooch crucible and potassium hydroxid, be further studied, with a view to its adoption as provisional.

(5) That the volumetric methods for tin devised by Baker, Alexander, and Bloomberg be further studied.

(6) That the methods for the determination of copper and zinc in food products be made the subject of study by this association as soon as possible.

HEAVY METALS IN FOODS: TIN.

SUPPLEMENTARY REPORT BY E. L. P. TREUTHARDT.

A study was made of the digestion of the sample by the use of nitric and sulphuric acids, and of six methods for determining tin. More or less complete results were obtained from seven collaborators.

DIGESTION OF SAMPLES.

The collaborators were requested to try the following methods upon various substances, to comment upon them, and to state which they considered best. Some of the workers omitted this work through lack of time, but gave their opinions as formed from previous experience.

METHODS.

1. Weigh 100 grams of the finely-ground sample into an 800 cc. Kjeldahl flask and add 50 cc. of concentrated sulphuric acid. Place the flask on a hot plate or on a wire gauze over a free flame; add about 30 cc. of concentrated nitric acid, raise the temperature to boiling and heat until white fumes are generated; then, without cooling, add 10 cc. of nitric acid and continue heating as before. Repeat the addition of nitric acid until the solution remains clear after boiling off the nitric acid fumes. The rapidity of digestion depends upon the temperature maintained—the higher the temperature the faster the material is oxidized.

2. Weigh out a 100-gram sample as before. Add 50 cc. of concentrated sulphuric acid and then at once 200 cc. of concentrated nitric acid. Boil down until the solution is clear. If the material chars badly, add more nitric acid; this will not be necessary in most cases.

3. Weigh out a 100-gram sample and add 100 cc. of concentrated nitric acid. Allow to stand, preferably overnight. If evolution of nitric fumes occurs, add more nitric acid, then add 50 cc. of concentrated sulphuric acid, allow to stand a few minutes (to see if any evolution of fumes takes place) as before, and then heat until white fumes are evolved. Proceed further as in *1*.

4. Proceed as in *3*, except before adding the sulphuric acid boil the nitric acid solution until the foaming ceases and the material boils quietly. Then add 25 cc. of concentrated sulphuric acid, allow the charge to clear a little, and add nitric acid a little at a time, proceeding as before. It is not necessary to allow to stand overnight.

5. Proceed as in *4*, but use 100 cc. of water and 150 cc. of concentrated nitric acid. Use 50 cc. of concentrated sulphuric acid.

This work evolves large quantities of corrosive fumes and ample hood space and good ventilation are essential. A flue similar to that used for nitrogen determinations is desirable. A very satisfactory flue can be made of asbestos paper painted with a mixture of barium sulphate ground with water glass solution. This is rolled upon bottles as molds while wet, and the bottles are pushed out before the mixture dries. After drying, holes may be cut into the flue, and sufficient connections may be made with asbestos pulp. After several coats of the silicate paint, the flue will last a long time.

CHOICE OF METHODS.

H. A. Baker: For gelatin and squash, Method *2*.

For sugar sirup, Method *3*, with further addition of 100 cc. of nitric acid. Time required, 7 to 8 hours.

E. Bloomberg: For vegetables, Method *4*.

For saccharine substances, Method *5*. If concentrated nitric acid is used, considerable frothing and foaming take place and in the majority of cases the product will go over. It is well to boil down and make several additions of nitric acid before adding the sulphuric acid and proceeding as before.

For animal and fatty matter, Method *1*.

R. W. Clough: Method *4*.

H. C. Fuller: Method *2*.

Method *1* is objectionable on account of frothing when nitric acid is first added. Fifty cc. of sulphuric acid and 200 cc. of nitric acid are used with beans, meat, etc., while 10 to 25 cc. of sulphuric acid and 50 to 100 cc. of nitric acid are used for products low in solids. After the first portion of nitric acid has boiled off, two additions of 5 to 25 cc. of nitric acid are sufficient.

E. L. P. Treuthardt: Method *3*, except for fatty substances, when Method *1* is better. In the latter, nitric acid is added to the cold solution.

H. E. Woodward: Method *1*, except for sugar sirups, when Method *3* is better. In the latter, 50 cc. of nitric acid is used instead of 100. Time required to digest 50 grams fish is 3 hours. Twelve additions of 10 cc. of nitric acid were made.

P. Rudnick and G. W. Trainor: Method *3* is the best all around method. Method *1* is perhaps next, with Method *5* following. Method *2* takes too long and Method *4* would be better using 50 cc. of sulphuric acid instead of 25.

Results obtained by Rudnick and Trainor.

SAMPLE	METHOD	TOTAL SULPHURIC ACID	TOTAL NITRIC ACID	10 CC. PORTIONS OF NITRIC ACID ADDED	TOTAL TIME
		cc.	*cc.*		*hours*
Canned baked beans (total solids 31 per cent):[1]	1	50	200	17	$1\frac{1}{4}$
	2	50	210	1	4
	3	50	210	11	$1\frac{2}{3}$
	4	25	230	13	$1\frac{5}{12}$
	5	50	220	7	$1\frac{5}{6}$
Canned sardines in oil:[2]	1	50	240	21	$1\frac{3}{4}$
	2	75	310	11	5
	3	50	380	28	$5\frac{1}{2}$
	4	50	290	19	$2\frac{1}{2}$
	5	50	290	14	$3\frac{1}{3}$
Canned strawberries (total solids 8.1 per cent):[3]	1	50	70	4	$1\frac{1}{4}$
	2	50	200	0	$5\frac{1}{2}$
	3	50	120	2	$1\frac{1}{4}$
	4	25	120	2	$1\frac{2}{3}$
	5	50	170	2	$2\frac{1}{12}$
Canned strawberries in heavy sirup (total solids 56.3 per cent):[4]	1	50	150	12	$1\frac{5}{8}$
	2	50	220	2	$4\frac{1}{4}$
	3	50	260	16	$1\frac{2}{3}$
	4	25	300	20	$1\frac{3}{4}$
	5	50	250	10	2
Canned corn beef:[5]	1	50	250	22	$1\frac{1}{12}$
	2	50	250	5	4
	3	50	220	12	$1\frac{5}{12}$
	4	50	240	14	$1\frac{7}{12}$
	5	50	250	10	$2\frac{1}{2}$

[1] Little or no trouble from frothing or bumping—Method *3* preferred.

[2] Hard product to handle; Method *5* preferred if any preference made.

[3] Product easily handled by any of the methods; Method *1* preferred if any preference made.

[4] Method *3* preferred; large amount of sugar necessitated use of much nitric acid; deficiency of sulphuric acid in Method *4* is particularly noticeable in this case.

[5] Method *3* preferred.

The following method calls for a preliminary extraction of the fat.

Digestion of fat-containing substances.—Place four 50-gram portions of the sample in 100 cc. tubes such as are furnished by the International Instrument Company with their large centrifuges. To each tube add 25 cc. of ordinary kerosene, stir well, centrifuge and decant off the supernatant oil through a filter into a beaker, taking care to get none of the subnatant sample into the filter. Repeat the extraction with two portions of 15 cc. and 10 cc., respectively, for each tube. Trans-

fer the extracted residues to two 800 cc. Kjeldahl flasks, combining the contents of two tubes into each digestion, and begin digestion by any method preferred. Transfer and combine the kerosene solution of the oil into two samples corresponding to their respective residues, which should be allowed to burn in porcelain crucibles, holding about 60 cc., using the filter, through which the solutions were filtered as a wick. To do this, fold the filter tightly and place it in the oil with the point up and ignite the point, add fresh portions of the oil-kerosene solution as the oil in the crucible burns away until all the solution has been burned off as completely as it will. Then ignite the crucible in a muffle or over a Méker type burner until all the carbon has been burned off. Add the residual ash to its respective digestion flask and continue the determination in the ordinary manner. It takes about 2 or 3 hours to burn off the kerosene, and no particular attention is required. The ash does not stick to the crucible if care is taken to select crucibles in which the inside glaze is not seriously damaged. The digestion is thus rendered very much easier and less troublesome, in fact, is practically as easy as the digestion of most of the fruits and vegetables.

DISCUSSION.

As very few of the collaborators agree upon what is the best method of digestion, it seems that no hard and fast procedure can be laid out, but that the details of the operation had best be left to the individual operators. It is evident that the treatment must vary according to the nature of the substance, and that improvements in the procedure will come by the devising of means to economize in reagents and in time. This method is least satisfactory in meat products or other substances containing much fat or oil. To prevent bumping, Bloomberg and Treuthardt use glass beads and Rudnick and Trainor use a 3-inch ring support completely covered by winding with $\frac{3}{8}$-inch asbestos cord.

DETERMINATION OF TIN.

METHODS.

Except in Method *4*, the sample is first digested to a colorless or pale yellow solution by one of the methods given under "Digestion of Sample."

1. Gravimetric method I.—Add 200 cc. of water to the digested solution and pour into a 600 cc. beaker. Rinse out the Kjeldahl flask with 3 portions of boiling water so that the total volume of the solution is about 400 cc.; allow to cool and add 100 cc. of concentrated ammonium hydroxid. This amount of ammonium hydroxid should render the solution nearly neutral, unless more than 50 cc. of sulphuric acid have been used for digestion. The solution should be tested to see that it is still somewhat acid. In case of large excess acid, add ammonium hydroxid until just alkaline and then make about 2 per cent acid with hydrochloric or sulphuric acid. Pass in a slow stream of hydrogen sulphid for an hour having the covered beakers on an electric hot plate at about 95°C. Allow to digest on a hot plate for an hour or two.

Filter the tin sulphid on a 11 cm. filter. Wash with 3 portions of wash solution alternated with 3 portions of hot water. The wash solution is made up of 100 cc. of saturated ammonium acetate, 50 cc. of glacial acetic acid, and 850 cc. of water. The filter papers used in this method are C. S. & S. No. 590, white ribbon.

Place the filter and precipitate in a 50 cc. beaker and digest with 3 successive portions of ammonium polysulphid, bringing to a boil each time and filtering through a 9 cm. filter; wash with hot water; acidify with acetic acid, digest on the hot plate

for an hour and filter through a double 11 cm. filter. Wash with 2 portions of wash solution alternated with hot water and dry thoroughly in a weighed porcelain crucible. Thorough drying is essential to the success of the determination. Ignite very gently at first and later at full heat of Bunsen flame; finally heat strongly with large burner, or Méker burner, having the crucible partly covered. Stannic sulphid must be gently roasted to the oxid, but the oxid may be heated strongly without loss due to volatilization.

Weigh the stannic oxid and convert to metallic tin by the factor 0.7881.

2. Gravimetric method II.—Precipitate with hydrogen sulphid as in 1. Filter the tin sulphid on a Gooch crucible under suction, and wash six times as before, filling the crucible each time. Transfer absestos mat and precipitate to a 300 cc. Erlenmeyer flask, add 100 cc. of 20 per cent potassium hydroxid and boil over a free flame for about 2 minutes. Filter into a 400 cc. beaker, using Gooch crucible and bell jar if possible, otherwise double white ribbon paper; wash with hot water until filtrate comes through colorless. The filtrate will have a volume of 200 or 300 cc. Add 20 cc. of concentrated hydrochloric acid, and then neutralize with concentrated hydrochloric acid from a burette. Add 1 cc. excess acid. Digest in a warm place, preferably overnight. Make sure that the solution is acid and filter through a Gooch crucible which has previously been washed, ignited and weighed. Wash alternately with ammonium acetate solution and hot water until free from chlorids. Dry, ignite and weigh.

3. Volumetric method I (Baker).—Tin, after wet combustion, is precipitated in the usual way by hydrogen sulphid. Filter this precipitate upon a Gooch crucible with a false bottom, using suction. Wash the precipitate a few times and then push the false bottom, asbestos pad, and tin precipitate into a 300 cc. Erlenmeyer flask. Remove all traces of precipitate from the inside of the crucible by means of a jet of hot water and a policeman. Use a minimum amount of water for washing. Add 100 cc. of concentrated hydrochloric acid and 0.5 gram of potassium chlorate to the flask. Boil for about 15 minutes, making about four more additions of potassium chlorate as chlorin is boiled out of the solution. The chlorate is best added with a small glass spoon. This insures complete breaking up and solution of the tin sulphid as well as the elimination of the sulphur. Wash the particles of potassium chlorate down from the neck of the flask and give a final boiling to remove the chlorin. Finally add about 1.5 grams of aluminum foil (free from tin) to dispel the last traces of chlorin.

The flasks, in duplicate, are attached to a large Kipp generator charged with pure marble and hydrochloric acid. The carbon dioxid passes through a scrubber and is then divided into two streams by means of a Y tube, each stream of carbon dioxid entering an Erlenmeyer flask by means of a bulbed tube passing through the rubber stopper of the flask and having its lower end near the surface of the liquid in the flask. The carbon dioxid leaves the flask by a second bulbed tube, the opening of which is near the top of the flask. This tube is connected to one about 10 inches long which is immersed in water about 8 inches deep. This gives a water seal to the delivery tube and a pressure against which the Kipp apparatus must work. It also obviates any violent flow of the gas when not desired and permits a gas pressure in the Erlenmeyer flask.

Pure seamless black rubber tubing and $\frac{3}{8}$ inch glass are used to form the connections specified. Enough water is added to the flasks to dilute the hydrochloric acid to about 30 to 40 per cent. After the flasks are connected, raise the tubes in the water seal cylinder so that the Kipp apparatus has practically no pressure to overcome. Allow carbon dioxid to run through for a few minutes. Drop the tubes to the bottom of the cylinder, creating a pressure in the flasks. Lift the rubber stoppers

of the flasks alternately about a dozen times, and pump out any air remaining in the flasks.

Slightly raise the stopper of one of the flasks and quickly drop about 2 grams of alüminum foil into the flask. The foil should be folded into a strip about 1 cm. wide and slightly bent so as to prevent it from striking directly on the bottom of the flask. The tin is quickly reduced to metallic form and a great deal of hydrogen is evolved. Raise the tubes in the cylinder to allow carbon dioxid to pass through and place the flasks upon electric hot plates, heated at the "high" stop. The aluminum disappears and the tin is changed to stannous chlorid. The acid strength of the solution will now be 25 to 30 per cent.

After boiling for a few minutes, remove the flasks from the hot plates and cool in ice water, while still under carbon dioxid insulation. Lower the tubes in the cylinder. When cool, disconnect the flasks one at a time, putting a glass plug into the carbon dioxid inflow. Wash out the tubes, rubber stopper, and sides of the flask with air-free water, add starch paste and titrate at once with hundredth-normal iodin.

If it is desired, titrate by the excess method, running an excess of hundredth-normal iodin into the flask while it is still connected with the carbon dioxid stream. Wash out the tubes and titrate the excess iodin with sodium thiosulphate.

The rubber connections should be washed with water after each determination.

REAGENTS.

Air-free water.—Dissolve 20 grams of sodium bicarbonate in 2 liters of boiled distilled water and add 40 cc. of concentrated hydrochloric acid. Make up fresh.

Hundredth-normal iodin.—1.27 grams of iodin and 2 grams of potassium iodid per liter of water. This should be standardized daily against tin solution, containing asbestos, and run through the above procedure, omitting the precipitation and boiling with hydrochloric acid and potassium chlorate.

Hundredth-normal sodium thiosulphate.—2.48 grams of sodium thiosulphate per liter of water.

Standard tin.—1 gram of tin dissolved in about 500 cc. of concentrated hydrochloric acid. Make up to 1 liter with water. 1 cc. = 1 mg. of tin.

4. Electrolytic method. (*Cushman and Wettengel*).—Place 50 grams of the pulped material in a 600 cc. beaker and bring to a slow boil with 50 cc. of concentrated hydrochloric acid and 25 cc. of concentrated nitric acid. Stir the mixture continuously and continue the boiling 5 minutes unless there is danger of foaming, in which case remove the flame and allow the material to digest for 10 minutes. Dilute the solution with about an equal quantity of water, make alkaline with strong ammonium hydroxid and add 25 cc. of saturated ammonium sulphid. Digest the mixture for a few minutes with thorough stirring and filter out all insoluble organic matter on a ribbed filter. Use about 150 cc. of wash water (boiling water containing a little ammonium sulphid) in 5 separate washings, making the total solution to 400 cc.

Electrolyze the solution hot, using 1.5 amperes at 6 volts. Use a rotating cathode. The end of the revolving spindle carries a rubber stopper over which a clean weighed platinum crucible is slipped. From 1 to 4 hours is necessary to complete an electrolytic run, 2 hours being generally sufficient except in cases where the tin content is very high. At the end of a run clean the crucibles by heating in a solution made by mixing 100 cc. of 10 per cent oxalic acid with 100 cc. of concentrated nitric acid.

5. Volumetric method II (*Alexander, Bloomberg, and Lourie*).—Destroy the organic matter by the usual nitric and sulphuric acid digestion. Cool the clear straw-colored liquid, add about 50 cc. of water; neutralize against phenolphthalein with saturated caustic soda solution; run in enough soda to just turn the color pink, then

reverse with 1 to 4 sulphuric acid until colorless. Boil for 5 minutes, filter, wash with hot saturated solution of sodium sulphate once or twice, then rinse out flask with a hot solution of 30 cc. of hydrochloric acid to 100 cc. of water, pouring through filter paper; use about 50 cc. for rinsing the flask, then punch hole in paper and wash sides down with the hot acid solution. This solution should be received in a 300 cc. Erlenmeyer flask. Add glass beads and one gram of antimony dust, boil for 2 minutes; while boiling, stopper the flask with a one-hole rubber stopper through which a bent glass tube passes, the lower end of which dips into a solution of sodium bicarbonate, prepared by diluting 2 parts of saturated solution with one part of water. Cool under faucet. When cold, remove stopper, add 10 cc. of starch solution and 15 cc. of saturated sodium bicarbonate and titrate with standard iodin solution.

6. Volumetric method III (Bloomberg).[1]—Digest sample as usual. When light yellow in color, make one more addition of nitric acid and take to fumes. Then add 10 grams of potassium sulphate and heat for 10 minutes to drive off all remaining nitric acid; cool, transfer to a 500 cc. Erlenmeyer flask with approximately 200 cc. of water; add 40 cc. of concentrated hydrochloric acid and 1 gram of powdered antimony. Proceed as in *5*.

Modifications of Methods.

Some of the collaborators did not obtain good results with certain methods until the procedures were modified. The results obtained by the modified methods are marked with the superior figure "[1]" in the table of results. The modifications reported are:

1. H. E. Woodward obtained low results when the tin sulphid was filtered hot. By allowing to stand and filtering cold, he obtained a set of higher results.

2. E. Bloomberg stated that after the caustic potash solution was acidified, hydrogen sulphid was passed into the solution, otherwise there was not as complete precipitation of tin. As it is not possible to wash asbestos free from alkali, paper pulp was used instead of asbestos in the Gooch crucible.

4. R. W. Clough could not get satisfactory results by this method and employed one in which *1* was followed up to the solution of the sulphid in ammonium sulphid. The ammonium sulphid solution was then electrolized with 2.5 amperes, at 8 to 10 volts, using a platinum dish as cathode and a rotating wire disk as anode. Silvery and adhering deposits were obtained.

Samples.

Samples A and B were synthetic samples having the following composition:

A:	*per cent.*	*B:*	*per cent.*
Gelatin	4.00	Sucrose	30.00
Sucrose	8.30	Tartaric acid	1.00
Phosphoric acid	0.50	Tannic acid	0.10
Sodium benzoate	0.20	Sodium benzoate	0.20
Sodium phosphate	0.20	Cream of tartar	0.50
Sodium chlorid	0.30	Sodium chlorid	0.05
Ferrous sulphate	0.05	Ferrous sulphate	0.03
Water	86.43	Water	68.09
Tin	0.02	Tin	0.0267

Sample C was a commercial canned squash. A large batch was thoroughly mixed and aliquot portions taken as samples.

[1] This method was not sent to all the collaborators; results were obtained by two analysts.

ANALYTICAL RESULTS.

Cooperative results of determination of tin.

(Mg. per kilogram)

SAMPLE AND ANALYST	METHOD 1	METHOD 2	METHOD 3	METHOD 4	METHOD 5	METHOD 6
A (tin content 200 mg. per kilogram):						
H. A. Baker	.....	.....	202. 202. 201. 200. 202.	.....	.....	.....
E. Bloomberg	201.7 204.8	10.6 208.0	214.6 219.4	.....	199.3 199.4	208.8 200.6
R. W. Clough	181.2 187.5 204.1	157.6 159.9	....	.....	.....	.....
H. C. Fuller	177.	.....	.....	188.	.....	.....
P. Rudnick and G. W. Trainor	217. 215.	....	199.3 197.5 199.3 197.5	.....	206. 205.	.....
E. L. P. Treuthardt	143. 132.	203. 194.	200. 175.	.....	201. 208.	36. 127.
H. E. Woodward	91. 69. [1]183. [1]177.	244. 239.	216. 217.	174. 180.	.....	.....
B (tin content 267 mg. per kilogram):						
H. A. Baker	.....	.....	287. 282. 283. 280. 276. 274. 276.	.....	.....	.....
E. Bloomberg	277.3 280.5	5.6 185.8 [1]274.2	283.2	.....	269.	271.4 273.7
R. W. Clough	.....	240.3 258.4	253.8 259.6	[1]257. [1]213.	.....	.....
H. C. Fuller	255.	....	....	268.	.....	.....
P. Rudnick and G. W. Trainor	279. 280.	.....	264.9 266.7 266.3 266.8	.....	274. 272.	.....
E. L. P. Treuthardt	178. 176.	171. 196.	261. 264.	.....	224.	246. 275.
H. E. Woodward	170. 95. [1]247. [1]249.	277. 226.	294. 264.	220. 228.	.....	.....
C (tin content unknown):						
H. A. Baker	.....	.....	306. 324. 312. 310.5 305.5 319.6 308.	.....	.....	.....

SAMPLE AND ANALYST	METHOD 1	METHOD 2	METHOD 3	METHOD 4	METHOD 5	METHOD 6
C (tin content unknown)—Continued						
E. Bloomberg	261.8 258.6	163.3 226.9 [1]267.9	255.2 250.	.....	249.6 265.4	266.6 269.
R. W. Clough	.....	290.8 262.4	278.1 278.1	.....	.....	.....
H. C. Fuller	285.	.....	.....	284.	.....	.....
P. Rudnick and G. W. Trainor	327. 329.	.....	323. 323. 307.3 308.3	.....	329. 329.	.....
E. L. P. Treuthardt	298. 288.	271. 278.	325. 309.	.....	223. 0	304. 216.
H. E. Woodward	273. 245. [1]279. [1]263.	306. 226.	283. 282.	212. 214.	.....	.....

[1] Modified procedure (See p. 256.)

Besides the regular samples, Rudnick and Trainor have submitted the following results which they obtained on analyzing samples containing known amounts of tin:

Results on samples containing known amounts of tin.

SUBSTANCE	TIN ADDED	TIN RECOVERED		
		Method 1	Method 3	Method 5
	mg.	*mg.*	*mg.*	*mg.*
Strawberry preserves	20	20.10	.....	.....
	15	.....	14.90	.....
	15	.....	14.90	.....
	10	11.00	10.83 10.55	10.08
		.....	10.20 10.30	10.08
Corned beef	10	10.16	10.27	10.69
	10	9.54	10.64	10.65
Fresh meat	5	.....	5.30	.....
	10	.....	10.20	.....
	15	.....	15.20	.....
	15	.....	15.30	.....

COMMENTS BY ANALYSTS.

Some of the comments have already been given under "Modifications of Methods."

E. Bloomberg considers Method *1* the most accurate, although his modification of Method *2* also gives satisfactory results. He had trouble with bumping of the hydrochloric acid solution containing potassium chlorate. Antimony was used instead of aluminum for the reduction. Method *6* which he proposes is more rapid than the others. In this method copper has no effect upon the titration when the solution contains one-third its volume of hydrochloric acid. It sometimes happens

that the digested solution after the addition of potassium sulphate contains a precipitate of metastannic acid. In this case the operation should be repeated.

R. W. Clough considers Method *3* the most satisfactory. The results by Method *1* were too low, probably due to too rapid combustion. Method *4* did not prove at all satisfactory; ammonium sulphid did not separate the tin completely; and the metal did not deposit satisfactorily from the electrolyte, being dark and easily rubbed from the dish. In some cases a deposit of iron was obtained as well as tin. In Method *1* the use of hydrochloric acid instead of acetic acid is recommended to acidify the ammonium sulphid solution, as the latter tends to result in colloidal tin sulphid.

P. Rudnick and G. W. Trainor prefer Method *3* or *5* when a great number of samples are to be run, but Method *1* for single determinations. The results from Method *2* as given are worthless.

E. L. P. Treuthardt prefers Method *3*. The results by Method *1* were too low and compared very unfavorably with previous work by this method. Method *4* has been found not to recover all of the tin. The results by Methods *5* and *6* are erratic, due to lack of experience. The use of aluminum is preferred to antimony as a reducing agent.

H. E. Woodward prefers Method *4* provided it gives correct results; otherwise, Method *3*. At first he had trouble with copper sulphid from the rotating spindle forming a black deposit on the tin, but this was remedied by the use of a glass tube. Sample C foamed during electrolysis and had to have ether dropped upon the solution. A current of 1.8 amperes at 4 to 5 volts was used.

DISCUSSION.

Method *3* is considered the best by four collaborators; Method *4*, by two (provided it be accurate); and Method *1*, by one. As second choice we have Methods *3*, *5*, *6*, *1*, and the modified *2*.

Allowing a deviation of 20 mg. per kilogram either side of the actual amount of tin present gives limit of 180 to 220 mg. of tin per kilogram in Sample A, and 247 to 287 mg. in Sample B. A count of the number of results falling within these limits on Samples A and B gives the following, having a variation of 20 mg. per kilogram:

Method *1*, 15 out of 21, or 72 per cent.
Method *2*, 7 out of 15, or 47 per cent.
Method *3*, 31 out of 33, or 94 per cent.
Method *4*, 3 out of 6, or 50 per cent.
Method *5*, 9 out of 10, or 90 per cent.
Method *6*, 5 out of 8, or 63 per cent.

Assuming Method *3* to have the least variation, the 19 results under this method in Sample C were averaged, giving an average of 300 mg. per kilogram. As the tin content was greater, a greater variation of ± 25 mg. was allowed, making the limits 275 and 325 mg. The number of results falling within these limits on Sample C was as follows:

Method *1*, 4 out of 9, or 44 per cent.
Method *2*, 3 out of 8, or 38 per cent.
Method *3*, 17 out of 19, or 90 per cent.

Method *4*, 1 out of 3, or 33 per cent.

Method *5*, 0 out of 6, or 0 per cent.

Method *6*, 1 out of 4, or 25 per cent.

In these tabulations the results obtained by Woodward in Method *1* (filtering hot) and by Bloomberg in Method *2*, revised are not counted.

These results confirm the opinions of the analysts that Method *3* is the most satisfactory.

The results by Method *1* were disappointing. With much previous work done by others with this method it has been found to check closely with the theoretical results. It seems that this method is worthy of further trial before condemning it.

Method *2* in the modified form should also be given further trial. It is highly desirable that some accurate gravimetric method be developed as the volumetric methods are not convenient in case only a few samples have to be examined.

Method *4* does not recover all of the tin. Until some method or extraction is devised which will recover all of the tin, it is safest to work exclusively upon the acid digestion of the sample.

Methods *5* and *6* look promising. Not much work has been done with them, but if they can be made to give results as consistent as those obtained by Method *3*, they will have a great advantage in speed.

THE DETERMINATION OF LEAD IN PHOSPHATE AND ALUM BAKING POWDERS.

By A. F. Seeker and H. D. Clayton.

The determination of lead in phosphate and alum baking powders can not be accomplished by a simple colorimetric process such as that employed for citric and tartaric acid and cream of tartar (Allen's *Com. Org. Anal.*, 1909, 4th ed., vol. 1, page 589) owing to the fact that upon rendering a solution of the baking powder alkaline, a precipitate forms. It is well known that lead sulphid is incompletely precipitated from solutions containing even very moderate amounts of free mineral acid, and for this reason gravimetric determinations based upon a precipitation of lead sulphid are rendered unavailable unless the concentration of acid hydrogen ions can be reduced to a minimum and the phosphates at the same time held in solution. After much experimentation a suitable agent for this purpose was found in ammonium citrate. When sufficient of this salt is present neither calcium nor aluminum phosphate will be precipitated from solution even if the mixture is made alkaline. In practice, however, owing to the presence of considerable iron in commercial baking powders, it is found advantageous to have a slight excess

of citric acid in the baking powder solution in order to prevent too copious precipitation of ferrous sulphid. The method in detail is as follows:

Treat 20 to 25 grams of the baking powder with about 25 cc. of water adding the latter in small portions until effervescence ceases. Then add 20 to 25 cc. of concentrated hydrochloric acid (depending upon the amount of baking powder taken) in small portions at a time, and digest on a steam bath until the solution is perfectly clear and limpid, or until a drop of the solution gives no reaction for starch with iodin and potassium iodid. Add sufficient solution of lead-free ammonium citrate to correspond to 20 to 25 grams of citric acid (the amount taken being exactly equivalent to the weight of baking powder employed),[1] and render slightly alkaline to litmus with 1 to 1 ammonium hydroxid, adding the latter a little at a time, and being careful to keep the solution cool during this operation. Dilute to about 400 to 500 cc., add 10 cc. of 10 per cent hydrochloric acid, cool to room temperature, saturate with hydrogen sulphid, and allow to stand overnight.[2] Filter, using suction if necessary, wash the precipitate with hydrogen sulphid water, and finally with a little water. Dissolve the precipitate by passing through the filter three 5 cc. portions of boiling 10 per cent hydrochloric acid followed by three 5 cc. portions of boiling 25 per cent nitric acid, collecting the filtrate in a 100 to 150 cc. beaker. Finally wash the filter with a little hot water, add 2 cc. of concentrated sulphuric acid to the filtrate and washings, and evaporate on a hot plate until fumes of sulphuric acid appear. The solution should now be practically colorless but if it is not so add a little nitric acid and again evaporate until fumes appear. Cool, add 10 cc. of water, warm gently for a short time to dissolve any ferric sulphate that may have separated out, cool again, add 20 cc. of alcohol and allow to stand overnight. Filter through a Gooch containing asbestos and wash with alcohol. Place the Gooch in a small beaker and moisten the contents with a few drops of concentrated ammonium hydroxid. Then pour 10 cc. of 50 per cent ammonium acetate solution into the crucible and allow it to stand for about 15 minutes. Remove the crucible from the beaker and carefully wash the bottom and sides with water allowing the washings to run into the beaker. By placing the lips over the top of the crucible, blow the solution still remaining in the crucible into the beaker; wash the crucible with a little water forcing the washings through the asbestos pad in the manner just described. Rinse the bottom of the crucible with a jet of water and fit it into a bell jar arranged for filtering by suction. Pass the ammonium acetate solution and

[1] This reagent may be prepared by dissolving 100 grams of citric acid in 100 cc. of hot water, cooling, adding a little at a time sufficient ammonium hydroxid to leave a slight excess, again cooling, and then saturating with hydrogen sulphid. Allow to stand overnight or until the sulphids have settled out, filter, boil the filtrate to expel excess of hydrogen sulphid and ammonia, cool, and make up to 200 cc. with water. Lead-free citric acid may be used instead of this solution but it has the disadvantage of causing a considerable evolution of heat in the subsequent neutralization with ammonia, resulting in a precipitation of calcium citrate.

[2] In some cases especially when a large amount of calcium phosphate is present or when the solution has not been sufficiently diluted a white precipitate of calcium citrate will settle out on standing. In such cases decant the supernatant liquid through a filter and dissolve the precipitate in a small amount of dilute hydrochloric acid, add an excess of ammonium citrate, cool, render slightly alkaline with ammonium hydroxid, cool, saturate with hydrogen sulphid, and allow to stand for 5 to 12 hours. The precipitated sulphids are then filtered off and treated as in the regular method. The material remaining on the filter from the liquid first decanted has in the meantime been washed with hydrogen sulphid water and dissolved in hot hydrochloric and nitric acids, the solution being finally combined with that from the second precipitate.

washings through the Gooch, filtering twice if necessary to secure a perfectly clear filtrate, and wash thoroughly with a little hot water. Acidify the filtrate with acetic acid, heat nearly to boiling, add an excess of potassium dichromate and allow to stand overnight. Filter through a small tared Gooch, wash the precipitated lead chromate with cold water, dry the crucible and contents by heating for 20 to 30 minutes on a hot plate, cool, and weigh as lead chromate.

The following nine determinations were made upon a commercial sample of phosphate baking powder selected for experimental purposes:

Determination of lead in a commercial sample of phosphate baking powder.

GRAMS OF SAMPLE TAKEN	GRAMS OF LEAD CHROMATE OBTAINED	GRAMS OF LEAD FOUND	LEAD CALCULATED TO MG. PER KILO
25	0.0008	0.00050	20
25	0.0005	0.00032	13
25	0.0008	0.00050	20
25	0.0008	0.00050	20
25	0.0007	0.00045	18
25	0.0009	0.00060	23
25	0.0008	0.00050	20
25	0.0008	0.00050	20
25	0.0005	0.00032	13

By adding known amounts of lead to the baking powder the following results were obtained:

GRAMS OF SAMPLE TAKEN	GRAMS OF LEAD CHROMATE OBTAINED	GRAMS OF LEAD OBTAINED	GRAMS OF LEAD ADDED	GRAMS OF LEAD ORIGINALLY PRESENT IN SAMPLE	PER CENT OF LEAD RECOVERED
20	0.0017	0.00110	0.00088	0.0004	86
20	0.0024	0.00154	0.00132	0.0004	90
20	0.0034	0.00220	0.00176	0.0004	102
20	0.0050	0.00320	0.00270	0.0004	103
20	0.0049	0.00310	0.00270	0.0004	100
25	0.0076	0.00490	0.00440	0.0005	100

A trial of the method upon a mixture composed of equal parts of sodium bicarbonate, starch and tricalcic phosphate to which a known amount of lead had been added resulted in the recovery of 90 per cent of the lead added.

The method has been in use in the New York Food and Drug Inspection Laboratory for almost two years and has been employed upon a large number of different samples by three analysts who have been able to check their own work and that of each other.

The association adjourned until Wednesday morning at 9 o'clock.

THIRD DAY.

WEDNESDAY—MORNING SESSION.

REPORT ON SEPARATION OF NITROGENOUS BODIES (MEAT PROTEINS).

By A. D. Emmett, *Referee.*[1]

For the continuation of the coöperative study made in 1912, samples of desiccated lean beef and high grade beef extract were sent out to the collaborators. The recommendations[2] of the association that pertain to the separation of nitrogenous bodies in meat and meat products, include this year total nitrogen, insoluble nitrogen, coagulable nitrogen, and creatin and creatinin.

INSTRUCTIONS FOR COÖPERATIVE WORK.

A. TOTAL NITROGEN.

Recommendations.—(1) That in Bulletin 107, Revised, page 108, 7(a), the following sentence be added to the Kjeldahl method and recognized as provisional: "If desired, 5 to 7 grams of potassium sulphate may be added in addition to the mercury of the Kjeldahl method, and no potassium permanganate be used." This modification should be designated as the Kjeldahl-Gunning-Arnold method.

Approved for final action as provisional in 1913.

(2) That the length of time of digestion with the Kjeldahl-Gunning-Arnold method be studied further, with a view of ascertaining whether $1\frac{1}{2}$ hours' digestion after clearing up is as complete as when digestion is carried on 4 hours by the Kjeldahl or Gunning method.

Approved for further study.

a. Meats.

Methods.—Use 0.4 to 0.5 gram by difference of the sample of desiccated meat and proceed as follows, making triplicate determinations in each case:

(1) Use the official Kjeldahl method (Bulletin 107, Revised, page 108, 7a), that is, sulphuric acid, mercury, and potassium permanganate. Digest for at least 4 hours.

(2) Use the Gunning method (Bulletin 107, Revised, page 108, 7a), that is, sulphuric acid and potassium sulphate. Digest for at least 4 hours.

(3) Use the Kjeldahl-Gunning-Arnold method, that is, in addition to the mercury, add 5 to 7 grams of potassium sulphate. Do not use any potassium permanganate at the end. Run 3 series in triplicate digesting them $1\frac{1}{2}$, $2\frac{1}{2}$, and 4 hours respectively, after the liquid has become clear and reached the final color.

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[1] Presented by P. F. Trowbridge.

[2] Bur. Chem. Cir. 108, p. 15.

In the case of each of the methods, when the solution has become clear, turn off the heat and after cooling 15 minutes carefully wash down the sides of the flask with a small quantity of ammonia-free distilled water. From time to time shake the flasks in order to rinse down any particles that may be adhering to the sides. If desired, the strength of the acid used in titration may be checked against the small quantity of standard acid sent out with the samples.

b. Beef extracts.

METHOD.—Weigh off (by difference) in triplicate about 7 grams of the sample of beef extract into 150 cc. beakers. Dissolve each in cold (20°C.) ammonia-free water. Transfer the solutions carefully to 250 cc. measuring flasks. Dilute each to the mark and mix thoroughly. Measure off from each flask for the total nitrogen determination 25 cc. in duplicate and proceed exactly as outlined under "Total Nitrogen (a)." Mix the sample thoroughly before each measuring.

Save the remainder of the solutions for the subsequent creatin and creatinin determinations D*b* and D*c*.

B. INSOLUBLE PROTEIN.

RECOMMENDATIONS (for meats only).—That in Bulletin 107, Revised, page 108, 7, (b), the following method be studied during the coming year with the idea of its being made optional for determining insoluble protein: Exhaust 7 to 25 grams of the sample (depending upon its moisture content) with 330 cc. of cold (15°C.) distilled water by making 11 successive extractions, 4 of 50 cc., 4 of 25 cc., and 3 of 10 cc., each. Make the extract up to 500 cc. and determine total soluble nitrogen in 50 cc. Deduct percentage of soluble nitrogen from the total and multiply difference by 6.25 for insoluble protein.

Approved for final action in 1913.

METHODS.—*Provisional method.*—Determine the insoluble protein nitrogen according to the provisional method (Bulletin 107, Revised, page 108, 7 (b)). Thoroughly exhaust 2 grams of the sample with cold water after extraction with ether, filter, and determine nitrogen in the insoluble residue as directed under A. TOTAL NITROGEN. Multiply the percentage of nitrogen so obtained by 6.25 for the percentage of meat fiber or insoluble proteids.

Use 0.6 to 0.7 gram in triplicate of the desiccated sample of meat. Determine the total nitrogen in the insoluble residue according to the Kjeldahl-Gunning-Arnold method, A *a* (3). Subtract the value from the corresponding total nitrogen found above. Reserve the filtrate or the water extract for the determination by the *Proposed optional method* under C.

Proposed optional method.—Prepare a water extract of the sample of meat according to the following plan: Weigh off (by difference) 3 lots of about 7 grams each of the desiccated meat into 150 cc. beakers; add 5 to 10 cc. of cold (15°C.) ammonia-free distilled water to each; stir and make a homogeneous paste; add to each beaker 50 cc. of the distilled water; stir every 3 minutes for 15 minutes and let the mixture stand for 2 to 3 minutes. Decant the liquid upon quantitative filters having one for each beaker. Collect the filtrates in 500 cc. measuring flasks; drain the beakers, pressing out the liquid from the meat residue with the aid of a glass rod. Add to the residues in the beakers 50 cc. of the cold water, stir for 5 minutes and after standing 2 to 3 minutes decant as before. In case a considerable portion of the meat is carried over into the filters, transfer it back with the aid of a glass rod. Repeat the extraction as above, using the following additional amounts of cold water

each time: 50, 50, 25, 25, 25, and 25 cc. After the last extraction transfer the entire insoluble portion to the filters and wash three times with about 10 cc. of water. After each extraction allow each extract to drain thoroughly before pouring the next one on the filter. Dilute each of the 3 extracts up to the mark. Take 50 cc. in duplicate from each extract and make the total nitrogen determinations on each by the Kjeldahl-Gunning-Arnold method. Subtract this value from the corresponding total nitrogen determination on the meat to obtain the insoluble nitrogen.

C. COAGULABLE PROTEIN.

Recommendation.—That in connection with recommendation under B (page 268) a comparative study be made of the method as given in Bulletin 107, Revised, page 108, 7 (d) with the following method: Evaporate 150 cc. of filtrate from B to about 40 cc. and nearly neutralize to litmus (paper), having it faintly acid. Heat on steam bath 5 minutes. Filter, wash, transfer paper and contents to flask, and determine nitrogen as "total nitrogen." In both methods use the same volume of the filtrate from B and bring to same neutrality.

Approved.

Omit the last sentence in the above recommendation.

Methods.—*Provisional method.*—Determine the coagulable nitrogen in triplicate in the filtrates from B. *Provisional method* according to the method given in Bulletin 107, Revised, page 108, 7 (d): Almost neutralize the filtrate from the insoluble protein, leaving it still faintly acid, boil until the coagulable proteins separate, filter, wash, transfer the filter paper and contents to a Kjeldahl flask, and determine nitrogen as directed under total nitrogen. Multiply the percentage of nitrogen obtained by 6.25 to obtain the percentage of coagulable protein.

Use the Kjeldahl-Gunning-Arnold method for nitrogen.

Proposed optional method.—Determine the coagulable nitrogen in triplicate in the extracts from *B*. *Proposed optional method* as follows: Take 150 cc. in duplicate from each of the 3 extracts. Transfer to 250 cc. Jena beakers; stir occasionally; evaporate on the steam bath to about 40 cc.; when down to this volume, if not already neutral or faintly acid to litmus (paper), add cautiously twentieth-normal sodium hydroxid and heat for 5 minutes. The coagulum should separate out at once leaving a clear liquid. Filter on quantitative paper, using if possible 589 S. and S. "Blue Ribbon." Wash the beakers thoroughly with hot water four times, taking special care to clean the sides of the beakers. Finally wash the coagulum on the filter three times. Transfer the coagulum with paper to nitrogen flasks and then remove any of the material adhering to the beakers with concentrated sulphuric acid, taking the usual 25 cc. of acid in 5 cc. portions for the purpose. Heat the acid in the beakers on a hot plate and with a glass rod see that every particle of the coagulum comes in contact with the hot acid. Transfer to the flask and cautiously use hot water to assist the complete transfer of the coagulated protein. Add the mercury and gently heat the flask on the nitrogen digester until the water is driven off and frothing ceases. Proceed as in the Kjeldahl-Gunning-Arnold method for nitrogen. Reserve the filtrate for D*b*, creatin.

D. CREATIN AND CREATININ.

Recommendation.—That further study be made of the method for determining creatin and creatinin in meat and beef extract, with the idea of referring it to the association for final action in 1913.

Approved for final action in 1913.

The use of Folin's method[1] with some of the modifications[2] that have been suggested from time to time is recommended.

a. Standard creatin solution.

Use in triplicate 25 cc. of the solution of creatin sent out with the samples; transfer to a 50 cc. measuring flask; add 10 cc. of twice-normal hydrochloric acid and mix. Hydrolyze in an autoclave at 117° to 120°C. for 20 minutes; allow the flask to cool somewhat, remove, and chill under running water. Partially neutralize the excess of acid with sodium hydroxid free from carbonates, by adding 7.5 cc. of the 10 per cent alkali; dilute to the mark and mix. Use 20 cc. to make a preliminary reading to ascertain what volume to use to get a reading of approximately 8 mm., and transfer it to a graduated 500 cc. flask. Add 10 cc. of 10 per cent sodium hydroxid and 30 cc. of saturated (1.2 per cent) picric acid. Mix and rotate for 30 seconds and let stand exactly 4½ minutes. Dilute to the mark at once with distilled water. Shake thoroughly and read in the Duboscq colorimeter,[3] comparing the color with the half-normal potassium bichromate solution, set at 8 mm. If the reading is too high or too low calculate the quantity to use to obtain a reading of about 8 mm.

It is desirable that the strength of the bichromate solution used be checked against the standard solution sent with the samples. To obtain the values divide 81 by the reading and multiply by the volume factor to get milligrams of creatinin. This value multiplied by 1.16 gives creatin which divided by weight of sample times 100 gives percentage of creatin.

b. Meats.

Determine the creatin only in the meat. Evaporate filtrates and washings from the heat coagulable nitrogen C. *Proposed optional method* to about 5 to 10 cc. Then transfer with the least possible amount of hot water to a 50 cc. measuring flask. Keep the volume below 30 cc. Add 10 cc. of twice-normal hydrochloric acid, mix, and proceed exactly as described under D*a*.

c. Beef extracts.

Creatinin.—Transfer about 5 cc. of the thoroughly-mixed solution prepared for A*b* to 500 cc. measuring flasks. Add 10 cc. of the 10 per cent sodium hydroxid solution and 30 cc. of the saturated picric acid solution; mix and rotate for 30 seconds; let stand exactly 4½ minutes, then dilute to the mark at once with distilled water. Shake thoroughly and read the depth of color after standing. If the reading is less than 7 or over 9.5, repeat, calculating the quantity of solution to use to get a reading of about 8 mm. Report results as per cent of creatinin.

Creatin.—Transfer 20 cc. of each of the solutions made for A*b* to 50 cc. measuring flasks and proceed as outlined for creatin under D*a*. Subtract from the combined creatinin value the equivalent of the preformed creatinin and multiply the difference by 1.16 to convert into creatin. Report results as percentage of creatin.

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[1] *Zts. physiol. Chem.*, 1904, v. *41*.

[2] Benedict and Myers, *Amer. J. Physiol.*, 1907, **18**: 406; Emmett and Grindley, *J. Biol. Chem.*, 1907, **3**: 491; Cook, F. C., *J. Amer. Chem. Soc.*, 1909, **31**: 673; Bur. Chem. Bul. 132, pp. 154–158.

[3] The use of Kober's shade and the painting of the plungers, as he suggested for the nephelometer assist in getting a sharper end point and relieve the eye strain.

RESULTS OF COÖPERATIVE WORK.

TABLE 1.

Determination of total nitrogen in meat and beef extract.
(Results expressed in per cent.)

ANALYST	DESICCATED MEATS					BEEF EXTRACT				
	Kjel-dahl 4 hrs.	Gun-ning 4 hrs.	Kjeldahl-Gunning-Arnold			Kjel-dahl 4 hrs.	Gun-ning 4 hrs.	Kjeldahl-Gunning-Arnold		
			1½ hrs.	2½ hrs.	4 hrs.			1½ hrs.	2½ hrs.	4 hrs.
C. R. Moulton, University of Missouri, Columbia, Mo.	12.31	12.18	12.32	12.42	12.39	[1]8.54	8.83	8.95	9.04	....
	12.31	12.15	12.47	12.31	12.44	8.89	8.87	8.91	8.87	....
	12.25	12.31	12.46	12.33	12.44	8.80	[1]8.55	....	8.93	....
T. C. Trescot, Bureau of Chemistry, Washington, D. C.	12.86	12.74	12.91	12.91	12.86	9.11	9.12	9.18	9.18	9.18
	12.86	12.74	12.86	12.91	12.91	9.22	9.10	9.22	9.27	9.27
	......	12.74	12.91	12.86	......	9.22	9.14	9.27	9.27	9.22
Paul Rudnick and G. W. Trainor, Armour and Co., Chicago, Ill.	13.06	13.21	13.12	13.21	13.14	8.98	8.96	8.98	9.06	9.11
	13.03	13.06	13.14	13.13	13.13	8.95	8.79	8.99	8.99	8.99
	......	......	......	......	......	9.04	9.04	9.00	9.00	9.00
W. B. Smith, Bureau of Animal Industry, Kansas City, Mo.	12.48	12.31	12.54	12.51	12.60	([2])	([2])	([2])	([2])	([2])
	12.35	12.12	12.53	......	12.49	....	....	....	....	....
A. D. Emmett and B. S. Davisson, University of Illinois, Urbana, Ill.	12.79	12.78	12.71	12.75	12.73	8.95	8.80	8.91	8.95	8.90
	12.78	12.71	12.76	12.67	12.72	8.93	8.80	8.92	8.90	8.95
	[1]12.86	12.76	12.76	12.67	12.74	8.96	8.79	8.95	8.89	8.92

Summary—Average of results of the triplicate determinations—1913.

Moulton	12.29	12.21	12.42	12.35	12.42	8.85	8.85	8.93	8.95	....
Trescot	12.86	12.74	12.89	12.89	12.88	9.18	9.12	9.22	9.24	9.22
Rudnick and Trainor	13.05	13.14	13.13	13.17	13.14	8.99	8.93	8.99	9.02	9.03
Smith	12.42	12.22	12.54	12.51	12.55	8.73	8.82	8.87	8.85	8.82
Emmett and Davisson	12.79	12.75	12.74	12.70	12.73	8.95	8.80	8.93	8.91	8.92
Grand Average	12.69	12.61	12.74	12.72	12.74	8.94	8.91	8.99	8.99	8.99

Summary of results reported in 1912.

Moulton	13.36	......	13.19	13.30	13.25	9.30	....	9.35	9.32	9.37
Emmett and Davisson	13.22	..	13.32	13.23	13.35	9.23	....	9.30	9.30	9.36
Rudnick and Trainor	......	......	......	......	......	9.43	......	9.49	9.54	9.52
Grand Average	13.29	......	13.25	13.26	13.30	9.32	....	9.38	9.39	9.42
Grand Average for 1912-1913.	12.85	......	12.89	12.88	12.90	9.08	......	9.13	9.14	9.18

[1] Omitted from average. [2] Reported only the average results.

COMPARISON OF METHODS FOR DETERMINING TOTAL NITROGEN.

Table 1 gives the data for the total nitrogen in the desiccated meat and in the beef extract, including the triplicate determinations made by each analyst. According to the summary of the data, the Kjeldahl-Gunning-Arnold method gave as good results as either the Kjeldahl or the Gunning method. The length of the time of digestion for the Kjeldahl-Gunning-Arnold method had little or no influence, that is, the percentage values were as high for the $1\frac{1}{2}$ hour digestion, after clearing up, as for the 4-hour period. In fact, taking the average of the data for all the analysts for this year's (1913) report, the values for the meat were slightly higher for the Kjeldahl-Gunning-Arnold method than for the other two methods, being for the $1\frac{1}{2}$ hour period, 12.74 per cent, for the $2\frac{1}{2}$ hour period, 12.72 per cent, and for the 4-hour period, 12.74 per cent, and by the Kjeldahl and Gunning methods 12.69 and 12.61 per cent respectively. The average data for the beef extract show the same relative difference between the methods.

Referring to the data for last year's (1912) report, in Table 1 it will be seen that they confirm the above findings and thus furnish further evidence that the Kjeldahl-Gunning-Arnold method gives very satisfactory results when compared with the Kjeldahl and Gunning methods.

It is evident that the data from the different laboratories do not agree very well. This is due in the main to the variation in the strength of the standard acid used in the titration. In the case of Rudnick and Trainor through a mistake they failed to make their determinations upon the sample of meat that was sent out to the other collaborators, and the results that they reported for meat were obtained upon another sample.

COMMENTS BY ANALYSTS.

QUESTION.—In the case of the Kjeldahl-Gunning-Arnold method, do you think there is any advantage in digesting for a longer time than $1\frac{1}{2}$ hours after the digestion has become clear in the case of either the meats or the beef extract?

Mr. Moulton: No advantage at all.

Mr. Rudnick: No, although for routine work, we prefer to require not less than 2 hours after digestion has come to final color, not because this is necessary in all cases, but because it is sure to cover the exceptional cases in general nitrogen work.

Mr. Smith: No.

Mr. Emmett: On account of the differences of opinion regarding the meaning of the phrase "digestion clearing up," it would be safer to continue the boiling for 2 hours after this point has been reached.

Mr. Trescot: One and one-half hours after clearing is enough. In the Gunning and Kjeldahl methods, it should be 4 hours.

(May 13, 1913) I have lately made a great many determinations of many different samples, checking the Kjeldahl-Gunning-Arnold method up against the official Gunning method, and find that it gives better results and in one-half the time. In this laboratory, the Kjeldahl-Gunning-Arnold method has been used for several years in preference to official Kjeldahl method. It is shorter and on the whole gives more concordant results.

TABLE 2.

Comparison of the provisional and proposed method for determining water-soluble, water-insoluble and heat coagulable nitrogen in meats.

(Results expressed in per cent.)

ANALYSTS	PROVISIONAL METHOD—BA			PROPOSED METHOD—BB		
	Total soluble[1]	In-soluble	Coagu-lable	Total soluble	In-soluble[1]	Coagu-lable
Moulton	1.84	10.51	Lost	1.62	10.73	0.24
	2.08	10.27	0.12	1.59	10.76	0.26
	1.65	10.70	0.12	1.55	10.80	[2]0.34
Cook	2.36	10.53	Lost	1.96	10.93	0.45
	2.49	10.40	Lost	1.88	11.01	0.45
	2.29	10.60	Lost	1.76	11.13	0.40
Rudnick and Trainor	2.24	10.93	Lost	2.11	11.06	0.62
	2.53	10.64	0.54	2.14	11.03	0.62
	1.92	11.25	Lost	2.06	11.11	0.60
Smith	1.80	10.74	Lost	1.72	10.82	0.23
	1.51	11.03	Lost	1.71	10.83	0.25
	....	......	....	1.69	10.85	0.28
Emmett and Davisson	1.90	10.80	0.48	2.03	10.67	0.56
	1.89	10.81	0.45	2.04	10.66	0.59
	1.90	10.80	0.41	2.00	10.70	0.55

Summary—Average of triplicate determinations.

Moulton	1.86	10.49	0.12	1.60	10.76	0.25
Cook	2.38	10.51	Lost	1.87	11.02	0.43
Rudnick and Trainor	2.23	10.94	0.54	2.10	11.07	0.61
Smith	1.65	10.88	Lost	1.70	10.83	0.24
Emmett and Davisson	1.90	10.80	0.45	2.02	10.68	0.57
Average	2.01	10.72	0.37	1.86	10.87	0.48

[1] Determined by difference. [2] Omitted from average.

In this table, it will be noted that the insoluble nitrogen was obtained directly in the provisional method and by difference in the proposed method. In making the study of the data it should be borne in mind that the triplicate determinations for both methods represent separate extractions.

Considering the results for the total water-soluble nitrogen, the triplicates show less variation by the proposed method than by the provisional one. This is due in part at least to the fact that the soluble nitrogen was obtained by difference in the latter case, and since the percentage of insoluble nitrogen is considerably greater than the soluble form, a permissible difference between triplicates in the former case might produce a very pronounced error in the latter case. For example, considering Mr. Moulton's data, the maximum and minimum percentages of insoluble nitrogen by the provisional method were 10.70 and 10.27 per cent respectively, a difference of 0.43 per cent, or in per cent of the average

of these two values, 4.1 per cent. Expressing this same difference, 0.43 per cent, in per cent of the corresponding average value of the soluble nitrogen, it amounts to 23.1 per cent.

From the summary of the data for insoluble nitrogen it is seen that the range between extreme values is greater for the provisional method than for the proposed one. The grand average shows that there is very little difference between the two methods. In some cases the analysts obtained higher results for the insoluble nitrogen by the proposed method while in others they obtained practically the same values. It would seem, therefore, that the use of the proposed method for determining insoluble nitrogen is more satisfactory than the present one, since it gives more accurate results for the soluble nitrogen and no less accurate results for the insoluble form. There is also another possible advantage in this method, namely, that it eliminates the ether extraction of the samples previous to making the water extract. This step, however, may be necessary in the case of very fat meats.

The data for the coagulable nitrogen are too few in the case of the provisional method. The summary of the results suggests that the values were higher for the proposed method. It is evident that there was a wide difference between the results of the different analysts, but one method seems to have no advantage over the other in this respect.

COMMENTS BY ANALYSTS.

QUESTION.—In the forms of water-soluble nitrogen in meat, how did the work proceed with both methods? Did you have any special difficulty with the water extraction, the separation of the coagulable nitrogen, or the determination of creatin?

Mr. Moulton: The manipulation was very easy in all cases. Extracting with ether, of course, took time.

Mr. Cook: The insoluble nitrogen was determined more quickly by the provisional method, due to the use of a smaller sample, I think. I was surprised to get more soluble nitrogen by this method than by the proposed one. In the proposed method any error in the nitrogen determination is multiplied ten times.

Mr. Rudnick: The proposed optional method is easier of manipulation because of the omission of the ether extraction.

Mr. Smith: The new method is more uniform in its general action.

Mr. Emmett: Since the data for the soluble nitrogen are as valuable as those for the insoluble form, and since the former results are always much smaller than the latter, the proposed method is the better one. With it, the soluble nitrogen is determined directly and thus the errors fall upon the insoluble nitrogen if determined indirectly. Further, the proposed method gives sufficient solution for determining the coagulable nitrogen and the creatin.

DETERMINATION OF CREATIN AND CREATININ IN MEAT AND BEEF EXTRACT BY FOLIN'S METHOD.

The object of this part of the coöperative work was to study the applicability of Folin's method of determining creatin and creatinin to meat

and meat products. There is no doubt but that this is the best method available at the present time for determining these two constituents in meats. Whether the method will give concordant results upon the same samples of meat by different chemists has not yet been answered.

For this year's coöperative work upon the subject, the following were sent to each of the chemists: (a) solution of standard creatin, made from Kahlbaum's best product; (b) solution of standard potassium dichromate; (c) sample of desiccated meat and (d) two samples of beef extract.

TABLE 3.

Creatin and creatinin in meat and beef extract.

(Results expressed in per cent.)

ANALYST	CREATIN IN DESICCATED MEAT	BEEF EXTRACT A		BEEF EXTRACT B		CREATIN IN 25 CC. OF STANDARD	DICHROMATE READING
		Creatin	Creatinin	Creatin	Creatinin		
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*mg.*	*mm.*
Moulton	1.51	1.85	5.95	1.48	4.93	21.0	([2])
	1.54	[1]2.31	5.87	1.79	5.20	23.4	...
	1.51	1.96	5.91	1.10	4.99	22.6	...
Cook	1.44	1.26	4.78	....	....	19.8	7.8
	1.40	1.33	4.93	....	....	19.8	8.1
	1.55	1.40	4.94	....	....	20.2	8.0
Rudnick and Trainor	1.66	1.80	6.63	1.90	6.64	21.3	7.8
	1.80	1.76	6.65	1.93	6.57	19.5	8.0
	1.87	1.88	6.62	1.91	6.60	19.4	7.9
Smith	1.53	1.22	5.56	....	....	21.9	8.0
	1.59	1.17	5.50	....	....	22.5	...
	1.55	1.19	5.65	....	....	[1]23.3	...
Emmett and Davisson	1.72	0.64	6.58	1.18	5.66	21.7	8.0
	1.66	0.70	6.64	1.20	5.69	21.4	8.0
	1.59	Lost	[1]6.90	....	5.76	21.1	7.9
V. C. Myers and M. S. Fine, Post-Grad. Med. School, New York, N. Y.	1.68	0.69	6.35	1.40	5.97	22.4	8.0
	1.68	0.70	6.36	1.23	5.95	22.4	...
	1.68	0.71	6.30	1.33	6.01	20.9	..

Summary—Average of triplicate determinations.

ANALYST	CREATIN IN DESICCATED MEAT	BEEF EXTRACT A Creatin	BEEF EXTRACT A Creatinin	BEEF EXTRACT B Creatin	BEEF EXTRACT B Creatinin	CREATIN IN 25 CC. OF STANDARD	DICHROMATE READING
Moulton	1.51	1.91	5.91	1.46	5.04	22.3	([2])
Cook	1.46	1.33	4.88	1.23	5.44	19.9	7.9
Rudnick and Trainor	1.78	1.81	6.63	1.91	6.60	20.1	7.9
Smith	1.36	1.19	5.57	....	....	22.2	8.0
Emmett and Davisson	1.66	0.67	6.61	1.19	5.70	21.4	8.0
Myers and Fine	1.68	0.70	6.34	1.32	5.98	21.9	8.0
Grand Average	1.57	1.27	5.99	1.40	5.75	21.3	8.0

[1] Omitted from average. [2] Used standard sent out.

The triplicate results of each chemist, as a rule, agree very well for the three samples. The summary of the data indicate that there were very marked differences between the laboratories. These may have been due to faulty technic or to possible errors in sampling the products.

TABLE 4.

Percentage deviation from the arithmetic mean.

ANALYST	CREATIN IN DESICCATED MEAT	BEEF EXTRACT A		BEEF EXTRACT B		CREATIN IN 25 CC. OF STANDARD
		Creatin	Creatinin	Creatin	Creatinin	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Moulton	3.8	50.4	1.3	4.3	3.6	4.6
Cook	7.0	4.7	18.5	12.1	5.4	6.6
Rudnick	13.5	42.4	10.7	36.1	14.8	5.6
Smith	13.5	6.3	7.1	....	....	4.2
Emmett and Davisson	5.7	47.2	10.4	15.0	0.9	0.4
Myers and Fine	7.0	44.9	5.8	5.7	4.0	2.8
Average	8.4	32.6	8.9	14.6	5.7	4.0

That this difference in these data is not due entirely to the sampling is evident from the results reported upon the standard creatin solution. Here there seems to be great variation, ranging from 19.9 to 22.3 per cent and averaging 21.3 per cent. Calculating the percentage deviation from the arithmetic mean for these data, Table 4 last column, it varied from 0.4 to 6.5 per cent averaging 4.0 per cent. In other words from these limited data representing the results from six different laboratories it appears that the errors in the Folin method for determining creatin in a standard solution averages about 4 per cent.

In order to obtain information regarding the possibility of the samples not being thoroughly representative, Beef extract B was sent out about 2½ months after the other samples had been forwarded. The necessity of asking for this further coöperative work became evident as soon as the results for the meat and the Beef extract A were reported.

In the case of Beef extract A, the directions did not specify that it should be mixed just previous to weighing the portion for analysis. With Beef extract B, the analysts were requested to mix it very thoroughly. This was done by first warming the extract slightly, and then stirring. It should also be stated that Beef extract B was taken from the same lot of beef extract as Beef extract A. The lot was warmed and very carefully mixed in both cases before sampling.

In comparing the corresponding data (Table 3) for these two samples of beef extract, it is seen that the results for Beef extract B show less variation between the different laboratories than do those of Beef extract A. This fact is brought out more clearly in Table 4 which gives the percentage deviation from the mean. The average values are: For creatin 32.6 and 14.6 per cent respectively for A and B, and for creatinin 8.9 and 5.7 per cent respectively. The latter value for creatinin is not far from that found for the standard creatin solution.

These data are significant and indicate that the portions that were weighed for analysis from Beef extract B were more representative than were those from Beef extract A. It would seem, therefore, that the variations in the data for A were due in part to a physical change in the sample after it was sent out, that is, crystalline bodies may have separated out to a greater or less extent. Here again it is evident that more data would assist greatly in arriving at a more definite conclusion as to the per cent of errors in the Folin method for determining creatin and creatinin in beef extracts.

The data for the creatin in the desiccated meat show less variation than in the beef extract. The sample of meat was naturally easier to mix, and being dried there was no possibility of having any such changes take place as might occur in beef extract. Even these data, however, do not agree as closely as one might expect. The minimum per cent of creatin was 1.36 and the maximum was 1.78, giving an average of 1.57 per cent for all the data. The percentage deviation varied from 3.8 to 13.5, averaging 8.4.

These results vary about as much as those that were reported last year, as the following data upon desiccated meat show:

Analyst	*Percentage of creatin*	*Percentage deviation*
Moulton	1.80	4.6
Cook	1.88	9.3
Rudnick and Trainor	1.50	7.0
Emmett and Davisson	1.69	1.7
Average	1.72	5.6

The average of the results for the two years' work, which represents the analysis of the distinct samples and the average of ten reports made in triplicate, gives a percentage deviation of 7.3. Allowing an average error of 4 to 5 for the standard creatin solution, the method seems to give fairly good results for creatin in meats.

From the above discussion upon the application of Folin's method for determining creatin and creatinin in meat products, it would seem that this method is fairly accurate for creatin in meats and for creatinin in beef extracts. While for creatin in beef extract, there is apparently a possibility for much variation. This variation may be due to several factors other than those mentioned, as temperature and the ability of the analysts to match the characteristic colors to the same degree. The data for the standard dichromate solution show a remarkable agreement, however, and indicate that it was possible to match this orange tint at 8 mm. on the scale without any apparent difficulty.

COMMENTS BY ANALYSTS.

Mr. Myers: In our opinion the sources of error in the estimation of creatinin or creatin by the Folin method ought not to amount to over 5 per cent under ordinary

conditions. When conditions are carefully controlled, it should be as low as 1 per cent. Much must depend, however, upon the ability of the individual to match the colors.

Mr. Rudnick: I am inclined to think that the most frequent source of difficulties in this work is the reading of the colors. I have seen but very few operators whose eyes were very sensitive to differences in orange no matter how sensitive they might be to red or yellow. Furthermore, the eye seems to tire very much more rapidly towards orange than toward other colors, so that an attempt to make a number of readings would, in my opinion, doubtless result in a gradual decrease of sensitiveness of the eye of the observer during the work, so that the last reading might be expected to be far less reliable than the first. I do not think that this is the only explanation for the great variation in results, but I feel that it is one deserving careful consideration.

RECOMMENDATIONS.

It would seem to the referee from the coöperative work that has been done during the past two years upon the points involved in this report, that the following recommendations should be made:

I. Meats and beef extracts.

(1) That the Kjeldahl-Gunning-Arnold method for determining total nitrogen in meat and beef extract should become official.

(2) That in Bulletin 107, Revised, page 108, 7a, Kjeldahl-Gunning-Arnold be inserted after the word Gunning, making the sentence read: "Employ either the Kjeldahl, the Gunning, or the Kjeldahl-Gunning-Arnold method. The digestion with sulphuric acid should be continued for at least 4 hours with the first two methods, and for 2 hours after the digestion has become clear with the last method."

(3) That the following description of the Kjeldahl-Gunning-Arnold method be given in an appropriate place in Bulletin 107, Revised: In addition to the mercury and sulphuric acid of the Kjeldahl method add 5 to 7 grams of potassium sulphate. Digest as usual, but do not add any potassium permanganate at the end. Continue the digestion for 2 hours after the liquid has become clear or $1\frac{1}{2}$ hours after the digest has reached the final color.

II. Nitrogenous bodies in meats and meat products.

(1) That in Bulletin 107, Revised, page 108 (b), the following method for determining insoluble and soluble protein in meat be made optional: Exhaust 7 to 25 grams of the sample (depending upon the moisture content) with 330 cc. of cold (15°C.) distilled water. Make 11 successive extractions—4 of 50 cc., 4 of 25 cc. and 3 of 10 cc. each. Dilute the entire extract to 500 cc. and determine the nitrogen in 50 cc. Deduct the percentage of nitrogen found from the percentage of total nitrogen in the sample and multiply the difference by 6.25 to obtain insoluble protein.

(2) That in Bulletin 107, Revised, page 108, 7 (d), the proposed method for determining the coagulable protein in meats be made optional. For description of method see page 269.

(3) That the Folin method for estimating creatin and creatinin in meat and beef extract be made official, the method as originally published by Folin being modified as given under Section D, page 269 of this report.

THE ESTIMATION OF GLYCERIN IN MEAT JUICES AND EXTRACTS.

By F. C. Cook.[1]

Fluid preparations of meat frequently contain added glycerin, cane sugar, alcohol, and foreign protein. The need for a quantitative method for the determination of glycerin in both semi-solid and fluid meat extracts and juices has led to much experimental work by the writer. A study of various solvents for the extraction of glycerin was begun at the suggestion of W. D. Bigelow several years ago and a preliminary report of the use of acetone and anhydrous copper sulphate in determining glycerin in meat extracts is given on page 42 of Bulletin 114 of the Bureau of Chemistry. At various times since then, as opportunity arose, the investigation has been continued. For the determination of glycerin in most substances, the acetin and the dichromate methods are the two most satisfactory processes available. While the writer was working with the acetone extraction method, the work of Shukoff and Schestakoff[2] appeared. These authors applied an acetone extraction method to such products as crude glycerins, soaps, and oil residue. The glycerin was extracted with anhydrous acetone in a Soxhlet apparatus after mixing the mass with anhydrous sulphate. The acetone was removed and the residue from the acetone extract weighed after drying to constant weight at 78° to 80°C. for 4 to 5 hours. The authors gave some very satisfactory results comparing this process with that of Hehner.

Benzene, chloroform, alcohol, gasoline, carbon tetrachlorid, and ether were all tried as glycerin solvents. Pure glycerin was found to be but slightly soluble in chloroform, benzene, and ether, and soluble in alcohol and acetone. The latter appeared to answer the requirements and was selected as the solvent. The details of the following method were worked out by adding known amounts of glycerin to meat and yeast preparations and recovering the glycerin.

Acetone extraction method.—Weigh approximately 2 grams of a solid or 5 grams of a liquid meat preparation in a small lead dish containing 20 grams of ignited

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[1] Submitted too late to be presented at the meeting.

[2] *Zts. angew. Chem.*, 1905, **18**: 294.

sand. Transfer the lead dish and its contents to a mortar containing more ignited sand and several grams of anhydrous sodium sulphate and mix thoroughly. Transfer the lead dish and the sand to a Soxhlet apparatus which has a piece of cotton placed in the side arm to prevent the siphoning over of sand, etc. Extract the entire mass with redistilled anhydrous acetone for 10 hours; distill the acetone, carefully removing the last trace by means of a vacuum pump; take up the glycerin in water, add a little silver nitrate, make to 100 cc. volume, let stand overnight, filter, and oxidize a portion of the filtrate according to the dichromate method of Hehner.

Test of the acetone method.—To test the accuracy of the acetone method, samples of meat and yeast extracts and fluid meat preparations of known glycerin content were examined. When a dilute meat preparation to which no glycerin was added, was tested by this method, a blank of practically zero was obtained. To these extracts known amounts of glycerin, determined by titration with dichromate according to the Hehner process, were added. With solid meat and yeast extracts a blank of 0.5 to 1.0 per cent was obtained in most cases.

The results in the table show that from 92 to 100 per cent of the added glycerin was recovered. There is a tendency for the results by this method to be low, the last traces of glycerin being extracted with difficulty. From 5 to 10 grams of fluid extracts of meat were used, the amounts of glycerin present and recovered per 100 cc. being indicated.

Results of glycerin determinations in meat preparations.

GLYCERIN PRESENT IN 100 CC.	GLYCERIN FOUND IN 100 CC.	GLYCERIN RECOVERED
gram	*gram*	*per cent*
0.293	0.270	92.15
0.293	0.279	95.22
0.971	0.920	94.70
0.971	0.940	96.80
0.252	0.244	96.80
0.583	0.583	100.00
0.583	0.583	100.00

Acetone extracts a little nitrogen, which is probably all amino nitrogen, and the silver precipitates part of it. Phosphotungstic acid was used following the silver treatment, but the results were not satisfactory. This method has also been applied to the estimation of glycerin in inking pads with some success, no thorough study of its application to these products having been made. The important point is to make a solution of the inking pad or other substance tested, taking an aliquot and thoroughly mixing with ignited sand and sufficient anhydrous sodium sulphate to remove all the water. The extraction of the glycerin is only satisfactory when the substance is finely divided. The presence of cane sugar does not render the method valueless, as it is but slightly soluble in acetone. No claim is made for an absolute method for extracting glycerin

from meat and similar extracts and juices. Approximate results, however, are obtained which are of value in indicating the amounts of glycerin present in various mixtures containing large amounts of organic material.

No report was made on the separation of nitrogenous bodies (milk and cheese). The following paper was read by L. L. Van Slyke:

A STUDY OF SOME CONDITIONS AFFECTING THE PRECIPITATION OF CASEIN.

By L. L. Van Slyke and O. B. Winter.[1]

A careful study was undertaken of certain conditions affecting the precipitation of casein in milk, in order to ascertain whether the present official method, using acetic acid as precipitant, is satisfactorily efficient. Of many points studied, only three are presented as follows: (1) Amount of acid used, (2) concentration of acid when added, and (3) effect of variation of temperature.

In each experiment were used 10 cc. of freshly-separated, pasteurized, skimmed milk and enough water to make (together with acid added) about 100 cc. Acetic acid was used in amounts varying from 30 to 240 mg. (equivalent to 5 to 48 cc. of tenth-normal acid, or approximately, to 0.3 to 2.4 cc. of 10 per cent acetic acid). Indication of effectiveness of results was based upon these points: Amount of casein precipitated, character of filtrate in respect to clearness, and rapidity of filtration. Generally speaking, highest quantitative results are obtained when the filtrate is clearest and filtration is most rapid.

(1) *Amount of acid used.*—In milks low in casein (less than 2 per cent), good results were not obtained when less than 72 to 90 mg. of acid were used (equivalent to 12 to 15 cc. of tenth-normal acid), while in the same milks equally good results were obtained with amounts of acid of 120 mg. and higher (equivalent to 20 cc. of tenth-normal acid). In some cases, when milk contains large amounts of casein (3 per cent or more), as much as 50 cc. of tenth-normal acetic acid (containing 300 mg. of acid) can be used with best results.

(2) *Concentration of acid when added.*—Comparative trials were made in which in one case the acid was added to the milk diluted to nearly 100 cc., and, in the other, the acid was diluted to 90 cc. and added to the undiluted milk. While the quantity of casein precipitated is the same in both cases, the precipitate is more flocculent and filters more rapidly when the acid is diluted before addition to the milk.

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[1] Read by H. S. Bailey.

(3) *Effect of variation of temperature.*—Generally speaking, equally good results are obtained at all temperatures between 18 and 42, when the same amounts of acid are used.

The work in general goes to show that the present method is satisfactory, but that the conditions of its efficiency are much more elastic than its present precise statement would lead one to suppose.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By H. E. Barnard, *Chairman.*[1]

(Food adulteration.)

COLORS.

It is recommended—

(1) That the investigations now under way be continued.

Approved.

SACCHARINE PRODUCTS.

It is recommended—

(1) That the method for the determination of solids in molasses and other sugar products, by means of the refractometer, using Geerlig's table of equivalents and temperature corrections, the results to be expressed as percentages calculated from the refractometer readings, be finally adopted as provisional.

Adopted, final action.

(2) That the suggestions of the associate referee for 1911 be continued for action in 1914 and that the associate referee for the coming year give these matters further study.

Approved.

FRUIT PRODUCTS.

It is recommended—

(1) That the study of the effect of uranyl acetate and ammonium molybdate respectively on the polarizations of malic and tartaric acids in the presence of known amounts of acetic acid be continued with the view of constructing tables from which the amounts of malic or tartaric acid present can be read when the change in optical rotation due to either reagent is known.

Approved.

(2) That the Yoder procedure for the estimation of malic and tartaric acids be studied in connection with the tables mentioned in the preceding recommendation.

Approved.

[1] Presented by C. D. Howard.

WINE.

It is recommended—

(1) That the proposed method for the determination of total tartaric acid, by B. G. Hartmann and J. B. Eoff, as given in the report of the associate referee, be further studied with regard to its applicability to red wines.

Approved.

(2) That the suggested use of the Rochelle salt addition instead of tartaric acid, as provided in the Hartmann and Eoff method, be further studied.

Approved.

BEER.

It is recommended—

(1) That Method 3 (in the associate referee's report), on the determination of phosphoric acid in beer by the addition of calcium acetate, and subsequent ashing, be adopted as a provisional method in place of the direct volumetric determination with uranium acetate.

Approved for final action in 1914.

(2) That the misprints and mathematical inaccuracies in Bulletin 107, Revised, as noted in the associate referee's report, be carefully investigated.

Approved and referred for future action to the general Committee on Recommendations of Referees.

DISTILLED LIQUORS.

It is recommended—

(1) That the Allen-Marquardt method for fusel oil determination (Bul. 107, Rev., p. 98, (b)) be modified as follows: In fourth line after "is collected," add "Whenever aldehydes are present in excess of 15 parts per 100,000, add to the distillate 0.5 gram of meta-phenylene diamin hydrochlorid, reflux for an hour, distill 100 cc., add 25 cc. of water and continue distillation until an additional 25 cc. is collected."

Approved for further study with collaboration.

(2) That the associate referee be directed to confer with chemists engaged in spirits analysis, to do such collaborative work as is necessary, and to submit at the next meeting a revised Allen-Marquardt method containing such changes in details and manipulation as experience justifies.

Approved.

VINEGAR.

It is recommended—

(1) That the modification of the method for reducing sugars, as designated in Circular 108, page 7, be finally adopted as provisional.

Adopted, final action.

(2) That Fincke's method for formic acid as applied to vinegar (Bul. 162, p. 81; Cir. 108, p. 8) be finally adopted as provisional.

Adopted, final action.

(3) That methods 1, 2, 3, 4, 7, 9, 12, and 18, as printed in the 1911 Proceedings (Cir. 108, pp. 8–9) be finally adopted as provisional.

Adopted, final action.

(4) That the other subjects designated by the last associate referee (Cir. 108, p. 8) be given further study.

Approved.

FLAVORING EXTRACTS.

It is recommended—

(1) That the results in the associate referee's report on known samples of vanilla extracts be submitted to the committee on standards for consideration in connection with such other results as are available in establishing standards.

Approved.

(2) That Folin's colorimetric vanillin method as described in the *Journal of Industrial and Engineering Chemistry*, volume 4, page 670, be further studied on extracts prepared in various ways, and on other products containing vanillin; especially in the presence of substances which would interfere in the provisional procedure; to test its value as a method for use in special cases where the gravimetric process is not applicable; and for confirmatory purposes.

Approved.

(3) That Wichmann's qualitative coumarin method be given further consideration in connection with Folin's colorimetric vanillin method and as a preliminary test.

Approved.

(4) That the slight modification of Howard's method for peppermint extract as given in the associate referee's report be adopted as a provisional method. That the applicability of this method to certain other extracts be studied, employing such modifications as may be necessary.

Approved for further study with a view to final adoption in 1914 as provisional for peppermint.

(5) That the method for the examination of ginger extracts (Bul. 137, p. 79) be made the subject of further study during the ensuing year.

Approved.

SPICES.

It is recommended—

(1) That the recommendations on condiments other than spices by the associate referee for 1911 (Cir. 90, p. 10) be referred to the associate referee on spices to report in 1914.

Approved.

MEAT AND FISH.

It is recommended—

(1) That on page 106 of Bulletin 107, Revised, under "XVII. Methods for the analysis of meat and meat products. 1. Identification of Species —Provisional," fourth line, after "melting point," "melting point of stearin by Belfield-Emery method" be inserted.

Adopted, final action as provisional.

(2) That Price's method (Cir. 108, p. 10) be made the official method for starch in meat food products in place of Mayrhofer's method (Bul. 107, Rev., p. 109, (b), (2)).

Approved for further study with a view to its final adoption as provisional in 1914.

(3) That Folin's aeration method, as given in the report of the associate referee be introduced as (g) Ammonia, on page 109 of Bulletin 107, Revised.

Approved for further study with the recommendation that the referee for 1914 compare this method with that described by the referee for 1912 (Cir. 108, p. 10).

(4) That under (e) Ammonia, page 115 of Bulletin 107, Revised, the following be substituted: Mix 1 gram of meat extract with 2 cc. of normal hydrochloric acid and wash into the Folin apparatus with about 5 cc. of water. Proceed as under (g) Ammonia, page 109.

Approved for further study.

(5) That the method for sugar as given on page 172 of the associate referee's report be studied.

Approved.

FATS AND OILS.

It is recommended—

(1) That the glycerin saponification method for the preparation of fatty acids for use in the titer test (Cir. 108, p. 11) be adopted as provisional.

Adopted, final action.

(2) That Emery's method for the detection of added beef fat and other solid fats in lard (U. S. Dept. Agr., Bureau of Animal Industry, Cir. 132) be adopted as a provisional method.

Adopted, final action.

(3) That the Bechi or silver nitrate test for cottonseed oil be discarded.

Adopted.

(4) That 75° in addition or instead of 100° for the determination of the specific gravity of high melting point fats be given further study, and a report be made in 1914.

Approved.

DAIRY PRODUCTS.

It is recommended—

(1) That the method proposed in 1911 (Bul. 152, p. 101; Cir. 90, p. 10) as applied to milk, evaporated milk, sweetened condensed milk, thin cream, and ice cream, be given further study with a view to final adoption as provisional in 1914.

Approved for final action in 1914.

(2) That the modification for rich cream (Cir. 108, p. 12) be given further study with a view to final adoption as provisional in 1914.

Approved for final action in 1914.

CEREAL PRODUCTS.

It is recommended—

(1) That the method of Bryan, Given, and Straughn (Cir. 71) for the estimation of soluble carbohydrates (results to be expressed as dextrose) be made a provisional method.

Approved for final action as provisional in 1914.

(2) That the method, on page 193 of the associate referee's report, for the estimation of acidity of water extract of flour be made an official method.

Approved for further study with a view to final action as provisional in 1914.

(3) That Recommendations (2), (4), and (5) on page 12 of Circular 108 be referred to the associate referee for the coming year for definite action.

Approved.

VEGETABLES.

It is recommended—

(1) That the associate referee for the coming year make determinations of the easily separable liquid in canned tomatoes, corn, and butterbeans, paying special attention to the size and kind of sieve and to the time allowed for drainage, and in the case of tomatoes to the effect of the age of the canned product on the amount of easily separable fluid.

Approved for further study.

COCOA AND COCOA PRODUCTS.

It is recommended—

(1) That the method for the determination of casein in milk chocolate (Bul. 162, p. 130) be adopted as provisional.

Referred to the associate referee for further study this year with respect to the effect of high temperatures in the process of manufacture.

(2) That the method for the determination of milk fat in milk chocolate (Bul. 152, p. 159) as reported last year, be adopted as provisional.

Adopted, final action.

(3) That the methods for crude starch in cocoa be given further study.
Approved.

TEA AND COFFEE.

It is recommended—

(1) That the Fuller method for the determination of caffein in tea and coffee be further studied with a view to improving the method of extraction and filtration.

Approved.

(2) That the Gorter method be further studied with a view to purifying the caffein with sodium carbonate solution for direct weighing.

Approved.

(3) That the modified Stahlschmidt method be given another trial for the determination of thein in tea.

Approved.

PRESERVATIVES.

It is recommended—

(1) That a further study of the Fincke method for formic acid with reference to roasted or partially caramelized substances as well as to the interfering substances mentioned by Fincke (*Biochem. Zts.*, 1913, **15**: 278) be made during the coming year.

Approved.

(2) That the collection of data regarding the amount of volatile reducing substances occurring in natural products as determined by the Fincke method be continued, and that natural products be examined qualitatively for formic acid in order that the value of a qualitative test in detecting added formic acid may be finally ascertained.

Approved for further study.

(3) That the natural occurrence of formic acid in food products be further investigated.

Approved.

HEAVY METALS IN FOODS.

It is recommended—

(1) That the methods for the determination of lead in baking powder and baking powder materials, which were studied this year, be made the subject of further study.

Approved.

(2) That the methods for the determination of arsenic, substantially as given in Circular 102 and in the *Proceedings of the Eighth International Congress of Applied Chemistry*, volume 1, page 9, be studied for another year.

Approved.

(3) That the procedure of digesting the sample by the use of nitric and sulphuric acids be further studied. In this connection it is desirable to

develop further the procedures applicable to meats and fish, in which the time required may be shortened and which will allow the use of a larger sample.

Approved and referred to the associate referee for the coming year for recommendations.

(4) That the gravimetric method for tin, including modifications using Gooch crucible and potassium hydroxid, be studied further with a view to its adoption as provisional.

Approved for final adoption as provisional in 1914.

(5) That the volumetric methods for tin, devised by Baker, Alexander, and Bloomberg, be studied further.

Approved and referred to the associate referee for the coming year for recommendations.

(6) That the methods for determination of copper in food products be made the subject of study by this association as soon as possible.

Approved.

(7) That the methods for the determination of zinc in food products be made the subject of study by this association as soon as possible.

Approved.

BAKING POWDER.

No recommendation by the committee as no report from referee was received.

H. W. Wiley, honorary president, in an address before the association, spoke of the progress of applied chemical science in this country as related to agriculture, of the power to control the effect of seasons on crops by scientific investigation and application of science, and of the splendid opportunity for efficient service by the association in the coöperative work of making standards.

REPORT OF COMMITTEE ON NOMINATIONS.

By R. J. Davidson, *Chairman.*

The committee on nomination of officers for the ensuing association year reported the following list of nominations: For president, E. F. Ladd, of North Dakota; for vice-president, C. H. Jones, of Vermont; for secretary, C. L. Alsberg, of Washington, D. C.; for additional members of the executive committee, J. D. Turner, of Kentucky, and W. F. Hand, of Mississippi.

The secretary was instructed to cast the unanimous ballot of the association for these officers.

REPORT ON DAIRY PRODUCTS.

By E. M. Bailey, *Referee.*

In the examination of milk serum by means of the immersion refractometer the acetic acid method of preparing the serum has been adopted as the provisional method. In view of the distinct advantages of the copper sulphate method of preparing milk serum, chief of which are the rapidity with which the serum can be obtained and the narrower range of readings given by whole milk it seems advisable at this time to recommend that the referee on dairy products for the ensuing year consider this method for the purpose of having it adopted as an optional provisional method in 1914.

RECOMMENDATION.

By G. E. Patrick.

We receive so many requests for methods of analysis of evaporated milk, that is, unsweetened condensed milk, that I think the association should have something definite on the subject, and I recommend, therefore, that there be inserted on page 122 of Bulletin 107, Revised, after the method for Cream, the following: "Condensed Milk (unsweetened). Dilute 40 grams of the homogeneous material with 60 grams of distilled water, proceed as directed under Milk and correct the results for dilution." And on the same page, I recommend that the word "Sweetened" be inserted before "Condensed Milk."

REPORT ON FEEDS AND FEEDING STUFFS.

By W. J. Jones, Jr., *Referee.*

The following subjects were assigned for investigation: (1) Effect of time of extraction on the determination of fat by the petroleum ether method; (2) Effect on the determination of fat of the use of petroleum ethers from different sources; (3) Effect of moisture on the determination of fat by the petroleum ether method.

The study of the proper factor for converting nitrogen into protein was left to the discretion of the referee. By agreement with the secretary, W. D. Bigelow, it was decided that if it was considered advisable to take up this subject it would be under the direction of an associate referee.

In addition to the three assigned investigations, work has been done on the length of time necessary to dry the extractions with petroleum ether and on the determination of fat by the official method, with absolute ether without drying samples, and with Squibbs ether containing approximately 3 per cent of alcohol.

Owing to the nature of the investigation and the difficulty encountered in securing petroleum ethers from different petroleums it was decided not to send out samples to collaborators, but to confine this work to the laboratory of the referee.

The moisture reported is the average of nine determinations secured by drying 2 grams of the sample in a steam bath in hydrogen for 5 hours.

Attempts to secure petroleum ether from different sources were unsuccessful owing to the fact that in most cases the fractionations desired were not made and when special arrangements were possible the difficulties of securing suitable containers and transportation made it practically impossible to procure the reagent. The only petrolic ethers secured were those used last year, one from Pennsylvania petroleum and the other pentane from Kansas petroleum. Eighty-six per cent of the Pennsylvania ether distilled below 65°C., the distillation beginning at 31°C.; 100 cc. gave a residue of 0.7 mg. Ninety-nine per cent of the pentane distilled below 65°C., the distillation beginning at 27½°C.; 100 cc. have a residue of 7 mg. In securing the results reported redistilled petrolic ether and pentane were used and no residue was found in the solvent.

Kahlbaum's c. p. ether distilled over metallic sodium, dehydrated in the laboratory for 2 weeks over fresh metallic sodium and redistilled from fresh metallic sodium was used for the official determinations.

All determinations of fat were made in the ordinary Soxhlet apparatus using an S. and S. fat free capsule to hold the sample. Extractions were made on an electrical heater giving a temperature of 76°C.

Twenty-three samples representing fourteen classes of feeding stuffs offered for sale in the general markets were selected and carefully prepared according to official methods, under the supervision of F. D. Fuller, as follows:

DESCRIPTION OF SAMPLES FOR COÖPERATIVE WORK.

(1) Continental gluten feed, composed of the dried residues from the distillation processes in the manufacture of liquor and composed of corn, oat malt, and barley malt.

(2) Old process linseed meal adulterated with 1.2 per cent of cottonseed meal.

(3) Choice cottonseed meal containing 43.1 per cent of crude protein.

(4) Compound feed composed of alfalfa and molasses.

(5) Compound feed composed of corn, oats, alfalfa meal, brewers' dried grains, malt sprouts, and molasses.

(6) Compound feed composed of corn, oats, alfalfa meal, grain screenings, and molasses.

(7) Old process linseed meal adulterated with 4.8 per cent of cottonseed meal.

(8) Cottonseed cake containing 37.3 per cent of crude protein.

(9) Cottonseed feed (meal and hulls) containing 22.3 per cent of crude protein.

(10) Old process linseed meal.

(11) Corn germ meal.

(12) Homeoline (corn germ meal).
(13) Brewers' dried grains (corn grits and barley malt).
(14) Brewers' dried grains (malted barley and rice).
(15) Hubinger's gluten feed.
(16) Union Starch and Refining Co.'s gluten feed.
(18) Linseed feed (meal from unscreened flaxseed).
(20) Compound feed composed of wheat and corn gluten, hominy feed, barley feed and sprouts, corn distillers' grains and cottonseed meal.
(21) Corn distillers' grains.
(22), (23), and (24) Corn products gluten feed.
(25) Wheat bran and screenings (small percentage).

EFFECT OF TIME OF EXTRACTION ON THE DETERMINATION OF FAT.

In studying the effect of different periods of extraction since the proposed method called for 3 hours' extraction, it was decided to make the different periods multiples of 3 and hence the samples were extracted 3, 6, 9 and 12 hours. The extracts were all dried 3 hours in a water bath at the temperature of boiling water (98°C.).

It will be noted from Table 1 that all the undried samples show an increase in the amount of extract with Pennsylvania petrolic ether for the period from 3 to 6 hours, the average increase being 0.2 per cent varying from 0.06 per cent for Sample 5 to 0.33 per cent for Sample 21. Twenty-two of the samples show an average increase from 6 to 9 hours of 0.10 per cent, making the total average increase for the 6 hours from 3 to 9 hours 0.29 per cent, ranging from 0.12 per cent for Sample 22 to 0.49 per cent for Sample 13. Seventeen of the samples show an average increase of 0.04 per cent for the period from 9 to 12 hours, while 6 show no variation.

All the dried samples show an average increase in the amount of extract for the first period of 0.16 per cent and an additional 0.09 per cent for the second period, making the total increase from 3 to 9 hours 0.25 per cent. Six of the samples show an average increase of 0.02 per cent from 9 to 12 hours.

In the pentane extraction only 2 periods, 3 and 9 hours, were used, resulting in 23 of the undried samples showing an average increase in amount of extract of 0.19 per cent and the dried samples 0.21 per cent, the range in the former being from 0.07 per cent in Sample 22 to 0.44 per cent in Sample 25 and in the latter from 0.06 per cent in Sample 8 to 0.38 per cent in Sample 25.

The additional amount extracted in all samples under the varying conditions and different reagents indicates that 3 hours' extraction in the ordinary Soxhlet apparatus is not sufficient to secure complete extraction for the classes of feeding stuffs represented. For this reason the other subjects for investigation are reported on the basis of 9 hours' extraction, which Table 1 shows to give maximum results.

TABLE 1. *Effect of time of extraction on the determination*

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample							Dried sample	
		3 hours' extraction	6 hours' extraction	9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	6 hours' extraction
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	6.72	10.85	11.08	11.16	11.16	+0.23	+0.08	0.00	10.92	11.04
		10.94	11.17	11.26	11.26	+0.23	+0.09	0.00	10.75	10.81
		11.07	11.28	11.38	11.38	+0.21	+0.10	0.00	10.69	10.72
		10.95	11.18	11.27	11.27	+0.23	+0.09	0.00	10.79	10.86
2	6.26	6.07	6.34	6.50	6.50	+0.27	+0.16	0.00	6.04	6.23
		6.08	6.33	6.45	6.45	+0.25	+0.12	0.00	6.14	6.28
		6.05	6.29	6.41	6.42	+0.24	+0.12	+0.01	5.98	6.03
		6.07	6.32	6.45	6.46	+0.25	+0.13	+0.01	6.05	6.18
3	5.45	10.14	10.43	10.48	.....	+0.29	+0.05	....	10.32	10.35
		10.25	10.52	10.67	10.71	+0.27	+0.15	+0.04	10.28	10.31
		10.36	10.56	10.68	10.68	+0.20	+0.12	0.00	10.22	10.38
		10.28	10.50	10.61	10.70	+0.22	+0.11	+0.02	10.27	10.35
4	4.89	0.46	0.59	0.68	0.71	+0.13	+0.09	+0.03	0.40	0.49
		0.44	0.58	0.66	0.68	+0.14	+0.08	+0.02	0.43	0.51
		0.45	0.58	0.68	0.68	+0.13	+0.10	0.00	0.42	0.51
		0.45	0.58	0.67	0.69	+0.13	+0.09	+0.02	0.42	0.50
5	4.02	2.62	2.77	2.91	2.91	+0.15	+0.14	0.00	2.70	2.77
		2.66	2.84	2.99	2.99	+0.18	+0.15	0.00	2.50	2.55
		2.63	2.78	2.91	2.91	+0.15	+0.13	0.00	2.63	2.70
		2.64	2.80	2.94	2.94	+0.06	+0.14	0.00	2.61	2.67
6	4.31	2.63	2.75	2.90	2.90	+0.12	+0.15	0.00	2.63	2.71
		2.55	2.71	2.87	2.88	+0.16	+0.16	0.00	2.55	2.67
		2.63	2.79	2.96	2.96	+0.15	+0.17	0.00	2.60	2.69
		2.61	2.75	2.91	2.91	+0.14	+0.16	0.00	2.59	2.69
7	7.62	6.47	6.62	6.77	6.77	+0.15	+0.15	0.00	6.42	6.55
		6.56	6.66	6.79	6.81	+0.10	+0.13	+0.02	6.50	6.60
		6.42	6.56	6.68	6.68	+0.14	+0.12	0.00	6.44	6.54
		6.48	6.61	6.75	6.75	+0.13	+0.14	0.00	6.45	6.56
8	7.67	6.61	6.76	6.88	6.88	+0.15	+0.12	0.00	6.47	6.53
		6.57	6.73	6.83	6.83	+0.16	+0.10	0.00	6.48	6.53
		6.34	6.56	6.66	6.66	+0.22	+0.10	0.00	6.33	6.48
		6.50	6.68	6.79	6.79	+0.18	+0.11	0.00	6.43	6.51
9	8.00	3.60	3.80	4.02	4.04	+0.20	+0.22	+0.02	3.76	3.92
		3.58	3.87	4.12	4.14	+0.29	+0.25	+0.02	3.60	3.78
		3.70	3.90	4.07	4.10	+0.20	+0.17	+0.03	3.50	3.65
		3.63	3.86	4.07	4.09	+0.23	+0.21	+0.02	3.62	3.78
10	7.63	9.04	9.41	9.56	9.58	+0.37	+0.15	+0.02	9.12	9.20
		9.32	9.53	9.67	9.70	+0.21	+0.14	+0.03	9.24	9.32
		9.22	9.42	9.56	9.58	+0.20	+0.14	+0.02	9.05	9.14
		9.19	9.45	9.60	9.62	+0.26	+0.15	+0.02	9.14	9.22

of fat (3 hours of drying extract.).

PETROLEUM ETHER					PENTANE					
Dried sample					Undried sample			Dried sample		
9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	9 hours' extraction	Gain or loss 3 to 9 hours ±	3 hours' extraction	9 hours' extraction	Gain or loss 3 to 9 hours ±
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
11.06	11.07	+0.12	+0.02	+0.01	10.98	11.15	+0.17	10.81	11.14	+0.33
10.81	10.81	+0.06	0.00	0.00	.....	.....	....	.....	.....	......
10.72	10.72	+0.03	0.00	0.00	11.16	11.20	+0.04	10.90	11.16	+0.26
10.86	10.87	+0.07	0.00	....	11.07	11.18	+0.11	10.86	11.15	+0.29
6.29	6.34	+0.19	+0.06	+0.05	5.92	6.00	+0.08	5.72	6.08	+0.36
6.28	6.32	+0.14	0.00	+0.04	....	....	....	....	....	....
6.04	6.08	+0.05	+0.01	+0.04	6.11	6.23	+0.12	5.80	6.10	+0.30
6.20	6.25	+0.13	+0.02	+0.05	6.02	6.12	+0.10	5.76	6.09	+0.33
10.44	.....	+0.03	+0.09	.....	10.07	10.39	+0.32	10.01	10.42	+0.41
10.39	.....	+0.03	+0.08	.....	.....	.....	.....	.....	.....	.....
10.45	10.45	+0.16	+0.07	.....	10.39	10.62	+0.23	9.99	10.30	+0.31
10.43	10.45	+0.08	+0.08	.....	10.23	10.51	+0.28	10.00	10.36	+0.36
0.49	0.49	+0.09	0.00	0.00	0.53	0.63	+0.10	0.46	0.58	+0.12
0.52	0.52	+0.08	+0.01	0.00	.....	.....	.....	.....	.....	.....
0.53	0.54	+0.09	+0.02	+0.01	0.58	0.67	+0.09	0.45	0.57	+0.12
0.51	0.52	+0.08	+0.01	.....	0.56	0.65	+0.09	0.46	0.58	+0.12
2.79	2.80	+0.07	+0.02	+0.01	2.69	2.76	+0.07	2.67	2.83	+0.16
2.56	2.58	+0.05	+0.01	+0.02	.....	.....	.....	.....	.....	.....
2.71	2.72	+0.07	+0.01	+0.01	2.76	2.86	+0.10	2.62	2.77	+0.15
2.68	2.70	+0.06	+0.01	+0.02	2.73	2.81	+0.08	2.65	2.80	+0.15
2.71	2.75	+0.08	0.00	+0.04	2.57	2.95	+0.38	2.57	2.79	+0.22
2.68	2.70	+0.12	+0.01	+0.02	....	....	....	....	....	....
2.70	2.75	+0.09	+0.01	+0.05	2.62	2.70	+0.08	2.72	2.94	+0.22
2.70	2.73	+0.10	+0.01	+0.03	2.60	2.83	+0.23	2.65	2.87	+0.22
6.55	6.55	+0.13	0.00	0.00	6.24	6.37	+0.13	6.27	6.34	+0.07
6.60	6.61	+0.10	0.00	+0.01	....	....	....	....	....	....
6.57	6.57	+0.10	+0.03	0.00	6.26	6.45	+0.19	6.30	6.38	+0.08
6.57	6.57	+0.11	+0.01	0.00	6.25	6.41	+0.16	6.28	6.36	+0.08
6.56	6.57	+0.06	+0.03	+0.01	6.55	6.71	+0.16	6.43	6.51	+0.08
6.53	6.53	+0.05	0.00	0.00	....	....	....	...	....	....
6.48	6.48	+0.15	0.00	0.00	6.57	6.82	+0.25	6.48	6.53	+0.05
6.52	6.52	+0.08	+0.01	0.00	6.56	6.77	+0.21	6.46	6.52	+0.06
3.97	3.97	+0.16	+0.05	0.00	3.43	3.64	+0.21	3.51	3.60	+0.09
3.82	3.82	+0.18	+0.04	0.00	....	....	....	....	....	....
3.71	3.71	+0.15	+0.06	0.00	3.41	3.69	+0.28	3.48	3.57	+0.09
3.83	3.83	+0.16	+0.05	0.00	3.42	3.67	+0.25	3.50	3.59	+0.09
9.23	9.23	+0.08	+0.03	0.00	9.02	9.17	+0.15	8.91	9.01	+0.10
9.36	9.36	+0.08	+0.04	0.00	....	....	....	....	....	....
9.20	....	+0.09	+0.06	....	9.09	9.25	+0.16	9.08	9.21	+0.13
9.26	9.30	+0.08	+0.04	0.00	9.06	9.21	+0.15	9.00	9.11	+0.11

TABLE 1—Continued. *Effect of time of extraction on the determination*

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample							Dried sample	
		3 hours' extraction	6 hours' extraction	9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	6 hours' extraction
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
11	5.98	8.92	9.10	9.27	9.29	+0.18	+0.17	+0.02	8.88	8.95
		8.91	9.09	9.24	9.23	+0.18	+0.15	−0.01	8.91	8.97
		8.89	9.08	9.10	....	+0.19	+0.02	....	8.89	8.96
		8.91	9.09	9.20	9.26	+0.18	+0.11	....	8.89	8.96
12	4.36	7.18	7.42	7.61	7.62	+0.24	+0.19	+0.01	7.15	7.26
		7.19	7.39	7.58	7.58	+0.20	+0.19	0.00	7.08	7.17
		7.36	7.51	7.66	7.67	+0.15	+0.15	+0.01	7.05	7.13
		7.24	7.44	7.62	7.62	+0.20	+0.18	0.00	7.09	7.18
13	6.98	2.75	3.04	3.32	3.32	+0.29	+0.28	0.00	2.37	2.54
		2.75	2.99	3.24	3.25	+0.24	+0.25	+0.01	2.17	2.42
		2.71	2.90	3.13	3.19	+0.19	+0.23	+0.06	2.19	2.46
		2.74	2.98	3.23	3.25	+0.24	+0.25	+0.02	2.24	2.47
14	7.72	5.78	6.01	6.20	6.24	+0.23	+0.19	+0.04	4.75	4.96
		5.78	5.99	6.17	6.21	+0.21	+0.18	+0.04	4.81	5.02
		5.81	6.04	6.21	6.27	+0.23	+0.17	+0.06	4.76	5.00
		5.79	6.01	6.19	6.24	+0.22	+0.18	+0.05	4.77	4.99
15	7.10	4.50	4.57	4.67	4.69	+0.07	+0.10	+0.02	3.67	3.80
		4.43	4.58	4.67	4.69	+0.15	+0.09	+0.02	3.61	3.78
		4.55	4.67	4.77	4.78	+0.12	+0.10	+0.01	3.82	3.99
		4.49	4.61	4.70	4.72	+0.12	+0.09	+0.02	3.70	3.86
16	6.70	4.89	5.03	5.15	5.17	+0.14	+0.12	+0.02	4.47	4.73
		4.96	5.04	5.15	5.16	+0.08	+0.11	+0.01	4.56	4.73
		4.96	5.09	5.23	5.25	+0.13	+0.14	+0.02	4.47	4.64
		4.94	5.05	5.18	5.19	+0.11	+0.13	+0.02	4.50	4.70
18	7.75	8.56	8.71	8.76	8.79	+0.15	+0.05	+0.03	8.39	8.60
		8.57	8.74	8.80	8.82	+0.17	+0.06	+0.02	....	....
		8.68	8.82	8.88	8.91	+0.14	+0.06	+0.03	8.35	8.56
		8.60	8.76	8.81	8.84	+0.16	+0.05	+0.03	8.37	8.58
20	6.35	3.95	4.20	4.29	4.37	+0.25	+0.09	+0.08	3.24	3.66
		3.96	4.21	4.31	4.38	+0.25	+0.10	+0.07	3.34	3.75
		3.86	4.11	4.21	4.29	+0.25	+0.10	+0.08	3.40	3.76
		3.92	4.17	4.27	4.35	+0.25	+0.10	+0.08	3.33	3.72
21	5.94	9.09	9.41	9.48	9.59	+0.32	+0.07	+0.11	8.22	8.62
		8.94	9.28	9.31	9.42	+0.34	+0.03	+0.11	8.25	8.67
		8.92	9.24	9.30	9.41	+0.32	+0.06	+0.11	8.39	8.80
		8.98	9.31	9.36	9.47	+0.33	+0.05	+0.11	8.29	8.70
22	9.19	3.65	3.76	3.77	3.86	+0.11	+0.01	+0.09	2.55	2.69
		3.67	3.80	3.80	3.80	+0.13	0.00	0.00	2.47	2.61
		3.65	3.78	3.78	3.78	+0.13	0.00	0.00	2.52	2.60
		3.66	3.78	3.78	3.81	+0.12	0.00	+0.03	2.51	2.63

of fat (3 hours of drying extract).

PETROLIC ETHER					PENTANE					
Dried sample					Undried sample			Dried sample		
9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	9 hours' extraction	Gain or loss 3 to 9 ± hours	3 hours' extraction	9 hours' extraction	Gain or loss 3 to9 ± hours
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
9.03	....	+0.07	+0.08	....	8.90	9.01	+0.11	8.87	8.99	+0.12
9.05	....	+0.06	+0.08	....	....	....	....	....	....	....
9.05	9.05	+0 07	+0 09	0.00	8.85	8.98	+0.13	8.81	8.97	+0.16
9.04	....	+0.07	+0.08	0.00	8.88	9.00	+0.12	8.84	8.98	+0.14
7.36	7.36	+0.11	+0.10	0.00	7.10	7.24	+0.14	7.03	7.16	+0.13
7.25	....	+0.09	+0.08	....	....	....	....	....	....	....
7.24	....	+0.08	+0 11	....	7.00	7.21	+0.21	7.08	7.22	+0.14
7.28	....	+0.09	+0.10	0.00	7.05	7.23	+0.18	7.06	7.19	+0.13
2.81	2.82	+0.17	+0.27	+0.01	2.56	2.97	+0.41	2.32	2.58	+0.26
2.70	2.71	+0.25	+0.28	+0.01	....	....	....	....	....	....
2.76	2.76	+0.27	+0.30	+0.00	2.50	2.88	+0.38	2.37	2.58	+0.21
2.76	2.76	+0.23	+0.19	0.00	2.53	2.93	+0.40	2.35	2.58	+0.23
5.22	5.22	+0.21	+0.26	+0.00	5.45	5.61	+0.16	4.97	5.31	+0.34
5.25	5.28	+0.21	+0.23	+0.03	....	....	....	....	....	....
5.23	5.23	+0.24	+0.23	+0.00	5.47	5.66	+0.19	4.99	5.29	+0.30
5.23	5.24	+0.22	+0.24	+0.01	5.46	5.64	+0.18	4.98	5.30	+0.32
3.95	3.96	+0.13	+0.15	+0.01	4.36	4.54	+0.18	4.08	4.30	+0.22
3.93	3.93	+0.17	+0.15	0.00	....	....	....	....	....	....
4.14	4.15	+0.17	+0.15	+0.01	4.28	4.40	+0.12	4.14	4.29	+0.15
4.01	4.01	+0.16	+0.15	0.00	4.32	4.47	+0.15	4.11	4.30	+0.19
4.84	4.85	+0.26	+0 11	+0.01	4.67	4.85	+0.18	4.64	4.76	+0.12
4.89	4.90	+0.17	+0.16	+0.01	....	....	....	....	....	....
4.78	4 78	+0.17	+0 14	....	4.65	4.82	+0.17	4.63	4.77	+0.14
4.84	4.84	+0.20	+0.14	....	4.66	4.84	+0.18	4.64	4.77	+0.13
8.81	8.81	+0.21	+0.21	....	8.16	8.35	+0.19	8.17	8.31	+0.14
....	....	....	....	....	....	....	....	....	....	....
8.71	8.71	+0.21	+0.15	....	8.10	8.28	+0.18	7.83	8.04	+0.21
8.76	8.76	+0.21	+0.18	....	8.13	8.32	+0.19	8.00	8.18	+0.18
3.80	3.80	+0.42	+0.14	....	3.53	3.73	+0.20	3.20	3.50	+0.30
3.91	3.91	+0.41	+0.16	....	....	....	....	....	....	....
3.90	3.90	+0.36	+0.14	....	3.54	3.75	+0.21	3.27	3.63	+0.36
3.87	3.87	+0.39	+0.15	....	3.54	3.74	+0.20	3.24	3.57	+0.33
8.76	8.76	+0.40	+0.14	....	8.78	9.08	+0.30	8.73	9.11	+0.38
8.78	8.78	+0.42	+0.11	....	....	....	....	....	....	....
8.93	8.94	+0.41	+0 13	+0.01	8.69	8.99	+0.30	8.53	8.96	+0.43
8.82	8.83	+0.41	+0.12	0.00	8.74	9.04	+0.30	8.63	9.04	+0.41
2.74	2.74	+0.14	+0.05	....	3.54	3.61	+0.07	2.78	2.98	+0.20
2.67	2.67	+0.14	+0.06	....	....	....	....	....	....	....
2.64	2.65	+0.08	+0.04	+0.01	3.44	3.51	+0.07	2.55	2.75	+0.20
2.68	2.69	+0.12	+0.05	....	3.49	3.56	+0.07	2.67	2.87	+0.20

TABLE 1—Continued. *Effect of time of extraction on the determination*

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample							Dried sample	
		3 hours' extraction	6 hours' extraction	9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	6 hours' extraction
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
23	5.64	3.47	3.71	3.77	3.88	+0.24	+0.06	+0.11	1.49	**1.74**
		3.51	3.76	3.83	3.90	+0.25	+0.07	+0.07	1.43	**1.66**
		3.38	3.65	3.74	3.83	+0.27	+0.09	+0.09	1.32	**1.55**
		3.45	3.71	3.78	3.87	+0.26	+0.07	+0.09	1.41	**1.65**
24	11.03	1.82	1.92	2.01	2.09	+0.10	+0.09	+0.06	1.37	**1.50**
		1.84	2.00	2.03	2.12	+0.16	+0.03	+0.09	1.22	**1.32**
		1.78	1.95	1.98	2.06	+0.17	+0.03	+0.08	1.15	**1.28**
		1.81	1.96	2.01	2.13	+0.15	+0.05	+0.12	1.31	**1.37**
25	9.26	3.75	4.07	4.28	4.29	+0.32	+0.21	+0.01	3.53	**3.94**
		3.77	4.09	4.30	4.31	+0.32	+0.21	+0.01	3.69	**4.09**
		3.81	4.10	4.32	4.32	+0.29	+0.22	0.00	3.50	**3.87**
		3.78	4.09	4.30	4.31	+0.31	+0.21	+0.01	3.57	**3.97**

EFFECT OF PETROLIC ETHERS FROM DIFFERENT SOURCES IN THE DETERMINATION OF FAT.

In comparing the extractions of the undried samples with Pennsylvania petrolic ether and pentane it is found that every sample shows an increase in the amount extracted by the former, the average for the 23 samples being 0.37 per cent varying from 0.02 per cent in Samples 4 and 8 to 1.78 for Sample 23. When the extractions on the dried samples are compared, however, the results are more conflicting since 14 show an average increase of 0.19 per cent with Pennsylvania petrolic ether, 8 an average increase of 0.18 per cent with pentane and one no change. Averaging the results from the entire 23 dried samples the petrolic ether shows an average increase over pentane of 0.06 per cent.

It is noted that the extractions of the dried samples do not compare with the results on the undried, since some samples of the former show exactly opposite results from the latter with the reagents. Sufficient checks were made on this part of the work to insure that the difference in results is not due to errors in manipulation.

The results in Table 2 show very clearly that appreciable differences in the amount extracted may result from the use of petroleum ethers boiling below 65°C. from the different sources when used on different kinds of feeding stuffs and that these differences may be materially affected by the moisture present in the sample and the character of the material extracted.

of fat (3 hours of drying extract.)

PETROLIC ETHER					PENTANE					
Dried sample					Undried sample			Dried sample		
9 hours' extraction	12 hours' extraction	Gain or loss 3 to 6 hours ±	Gain or loss 6 to 9 hours ±	Gain or loss 9 to 12 hours ±	3 hours' extraction	9 hours' extraction	Gain or loss 3 to 9 hours ±	3 hours' extraction	9 hours' extraction	Gain or loss 3 to 9 hours ±
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1.84	1.84	+0.25	+0.10	....	1.83	2.05	+0.22	1.44	1.70	+0.26
1.74	1.74	+0.23	+0.08	....	....	....	....	....	....	...
1.68	1.68	+0.23	+0.13	....	1.71	1.95	+0.24	1.49	1.76	+0.27
1.75	1.75	+0.24	+0.10	....	1.77	2.00	+0.23	1.47	1.73	+0.26
1.53	1.53	+0.13	....	....	0.88	0.94	+0.06	0.80	0.93	+0.13
1.34	1.34	+0.02	....	....	....	....	....	....	....	...
1.32	1.32	+0.04	....	....	0.80	0.90	+0.10	0.76	0.91	+0.15
1.40	1.40	+0.06	....	....	0.84	0.92	+0.08	0.78	0.92	+0.14
4.01	4.03	+0.41	+0.07	+0.02	3.63	4.09	+0.46	3.57	3.95	+0.38
4.22	4.23	+0.40	+0.13	+0.01	....	....	....	....	....	...
3.99	4.00	+0.37	+0.12	+0.01	3.63	4.04	+0.41	3.66	4.04	+0.38
4.07	4.09	+0.40	+0.10	+0.02	3.63	4.07	+0.44	3.62	4.00	+0.38

EFFECT OF MOISTURE ON THE DETERMINATION OF FAT.

Comparison of the extractions of undried and dried samples shows with both Pennsylvania petrolic ether and pentane appreciable increases in the amounts extracted from the undried samples. With Pennsylvania petrolic ether all 23 samples show an increase ranging from 0.05 per cent for Sample 18 (linseed feed) to 2.03 per cent for Sample 23 (gluten feed) with an average increase from the undried samples of 0.45 per cent. In the pentane extractions the increase between the undried and dried samples is less pronounced ranging from 0.01 per cent for Sample 5 to 0.69 per cent for Sample 22 (gluten feed) with an average increase for 20 samples of 0.15 per cent, one sample, No. 6, showing an increase of 0.04 per cent and two, Nos. 21 and 24, no variation.

The greatest effect of moisture seems to be exerted in the Pennsylvania petrolic ether extractions of brewers' grains, distillers' grains, gluten feeds, and compound feeds containing one or more of these products. With pentane no special difference is noted except in the case of brewers' grains, Sample 13 (corn grits and barley malt), and gluten feeds, Samples 22 and 23.

While the fact that all of the samples with Pennsylvania petrolic ether and all but one with pentane show an increased amount of extract when used on the undried samples as compared with the dried, a study of the results gives no indication of any ratio between the amount of moisture

TABLE 2.

Effect of petrolic ethers from different sources on the determination of fat.
(9 hours' extraction; 3 hours' drying)

SAMPLE NO.	MOISTURE	UNDRIED SAMPLE			DRIED SAMPLE		
		Pennsylvania petrolic ether	Kansas pentane	Difference petrolic ether and pentane ±	Pennsylvania petrolic ether	Kansas pentane	Difference petrolic ether and pentane ±
	average per cent	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*
1	6.72	11.16	11.15	....	11.06	11.14	....
		11.26			10.81		
		11.38	11.20		10.72	11.16	
		11.27	11.18	+0.09	10.86	11.15	−0.29
2	6.26	6.50	6.00	....	6.29	6.08	....
		6.45			6.28		
		6.41	6.23		6.04	6.10	
		6.45	6.12	+0.33	6.20	6.09	+0.11
3	5.45	10.48	10.39	....	10.44	10.42	....
		10.67			10.39		
		10.68	10.62		10.45	10.30	
		10.61	10.51	+0.10	10.43	10.36	−0.07
4	4.89	0.68	0.63	....	0.49	0.58	....
		0.66			0.52		
		0.68	0.67		0.53	0.57	
		0.67	0.65	+0.02	0.51	0.58	−0.07
5	4.02	2.91	2.76	....	2.79	2.83	....
		2.99			2.56		
		2.91	2.86		2.71	2.77	
		2.94	2.81	+0.13	2.69	2.80	−0.11
6	4.31	2.90	2.95	....	2.71	2.79	....
		2.87			2.68		
		2.96	2.70		2.70	2.94	
		2.91	2.83	+0.08	2.70	2.87	−0.17
7	7.62	6.77	6.37	....	6.55	6.34	....
		6.79			6.60		
		6.68	6.45		6.57	6.38	
		6.75	6.41	+0.34	6.57	6.36	+0.21
8	7.67	6.88	6.71	....	6.56	6.51	....
		6.83			6.53		
		6.66	6.82		6.48	6.53	
		6.79	6.77	+0.02	6.52	6.52	0.00
9	8.00	4.02	3.64	....	3.97	3.60	....
		4.12			3.82		
		4.07	3.69		3.71	3.57	
		4.07	3.67	+0.40	3.83	3.59	+0.24
10	7.63	9.56	9.17	....	9.23	9.01	....
		9.67			9.36		
		9.56	9.25		9.20	9.21	
		9.60	9.21	+0.39	9.26	9.11	+0.15

TABLE 2—Continued.

SAMPLE NO.	MOISTURE	UNDRIED SAMPLE: Pennsylvania petrolic ether	UNDRIED SAMPLE: Kansas pentane	UNDRIED SAMPLE: Difference petrolic ether and pentane ±	DRIED SAMPLE: Pennsylvania petrolic ether	DRIED SAMPLE: Kansas pentane	DRIED SAMPLE: Difference petrolic ether and pentane ±
	average per cent	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*
11	5.98	9.27	9.01	....	9.05	8.99	....
		9.24			9.03		
		9.10	8.98		9.05	8.97	
		9.20	9.00	+0.20	9.04	8.98	+0.06
12	4.36	7.61	7.24	....	7.25	7.16	...
		7.58			7.24		
		7.66	7.21		7.36	7.22	
		7.62	7.23	+0.39	7.23	7.19	+0.04
13	6.98	3.32	2.97	....	2.81	2.58	....
		3.24			2.70		
		3.13	2.88		2.76	2.58	
		3.23	2.93	+0.30	2.76	2.58	+0.18
14	7.72	6.20	5.61	....	5.22	5.31	....
		6.17			5.25		
		6.21	5.66		5.23	5.29	
		6.19	5.64	+0.55	5.23	5.30	−0.07
15	7.10	4.67	4.54	....	3.95	4.30	....
		4.67			3.93		
		4.77	4.40		4.14	4.29	
		4.70	4.47	+0.23	4.01	4.30	−0.29
16	6.70	5.15	4.85	....	4.84	4.76	....
		5.15			4.89		
		5.23	4.82		4.78	4.77	
		5.18	4.84	+0.34	4.84	4.77	+0.07
18	7.75	8.76	8.35	....	8.81	8.31	....
		8.80					
		8.88	8.28		8.71	8.04	
		8.81	8.32	+0.49	8.76	8.18	+0.58
20	6.35	4.29	3.73	....	3.80	3.50	....
		4.31			3.91		
		4.21	3.75		3.90	3.63	
		4.27	3.74	+0.53	3.87	3.57	+0.30
21	5.94	9.48	9.08	....	8.76	9.11	....
		9.31			8.78		
		9.30	8.99		8.93	8.96	
		9.36	9.04	+0.32	8.82	9.04	−0.22
22	9.19	3.77	3.61	....	2.74	2.98	....
		3.80			2.67		
		3.78	3.51		2.64	2.75	
		3.78	3.56	+0.22	2.68	2.87	−0.19

TABLE 2—Continued.

SAMPLE NO.	MOISTURE	UNDRIED SAMPLE: Pennsylvania petrolic ether	UNDRIED SAMPLE: Kansas pentane	UNDRIED SAMPLE: Difference petrolic ether and pentane ±	DRIED SAMPLE: Pennsylvania petrolic ether	DRIED SAMPLE: Kansas pentane	DRIED SAMPLE: Difference petrolic ether and pentane ±
	average per cent	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*
23	5.64	3.77 3.83 3.74	2.05 1.95	....	1.84 1.74 1.68	1.70 1.76	....
		3.78	2.00	+1.78	1.75	1.73	+0.02
24	11.03	2.01 2.03 1.98	0.94 0.90	....	1.53 1.34 1.32	0.93 0.21	....
		2.01	0.92	+1.09	1.40	0.92	+0.48
25	9.26	4.28 4.30 4.32	4.09 4.04	....	4.01 4.22 3.99	3.95 4.04	....
		4.30	4.07	+0.23	4.07	4.00	+0.07

present and the increase in extract, hence while it is apparent that the presence of moisture affects the determination the amount of this effect is more largely controlled by the nature of the material extracted than by the amount of moisture present at least when this does not exceed 8 per cent. It is also apparent that the extracting power of petrolic ethers from different sources at least of the two used in this investigation is not affected to the same degree by the moisture present in the sample.

OFFICIAL COMPARED WITH PETROLIC ETHER METHOD.

Comparing the results with the proposed petrolic ether method (3 hours' extraction) and the official method all the samples except two, 18 and 24, show an appreciable increase in the amount extracted by the latter ranging from 0.10 per cent for Sample 10 to 1.53 per cent for Sample 1, with an average increase for the 21 samples of 0.62 per cent. The most pronounced differences are shown by the distillers' and brewers' grains and compounded feeds containing them, although Sample 25 (wheat bran and screenings) gives a difference of 0.97 per cent. In the case of cottonseed products appreciable differences are found in that Sample 3, choice cottonseed meal, shows an increase by the official method of 0.49 per cent, Sample 8, good cottonseed meal, 0.64 per cent and Sample 9, cottonseed feed (meal and hulls), 0.34 per cent.

No reason was apparent for the failure of Samples 18 and 24 to follow the general rule of decreased amount of extract with petroleum ether the former showing an increase of 0.04 per cent and the latter 0.16 per cent.

When the petroleum ether extraction is continued for 9 hours the differences are not so large and in six of the samples 2, 7, 9, 10, 18, and 24 the extraction with petroleum ether has increased so that it exceeds that of absolute ether. Seventeen of the samples show an average excess by the official method of 0.40 per cent ranging from 0.02 per cent for Sample 22 to 1.21 per cent for Sample 1. Six samples show an average excess for petroleum ether of 0.20 per cent ranging from 0.04 per cent for Sample 7 to 0.36 per cent for Sample 24.

COMPARISON OF RESULTS OBTAINED BY THE USE OF ABSOLUTE ETHER ON DRIED AND UNDRIED SAMPLES.

From Table 3 it is seen that in comparing the official method with the method of extracting the sample with absolute ether, without previously drying, increases in the amount of extract are obtained in the case of 12 of the undried samples. These increases vary from 0.03 per cent in the case of Sample 9 to 1.29 per cent in Sample 21 with an average increase of 0.49 per cent. In 11 of the samples slightly higher results were secured by the official method on the dried samples, the increases varying from 0.01 to 0.29 per cent with an average increase of 0.13 per cent. In Samples 1 and 21, which are distillery by-products the increase of extract obtained from the undried samples is very marked, being 1.11 and 1.29 per cent, respectively, while with the other samples the range is from 0.03 to 0.60 showing that the nature of the material under examination affects the quantity of extract secured from the undried condition as compared with that obtained by the official method.

In comparing the relative value of different feeding materials it is essential that a moisture-free basis should be secured and it seems advisable from the results of investigation to continue the extraction of the crude fat from the moisture-free substances. This is especially necessary in order to compare the work of different analysts on the same basis.

EXTRACTION WITH SQUIBBS ETHER AS COMPARED WITH OFFICIAL METHOD.

In view of the fact that the official method requires the use of ethyl ether free from water and alcohol, it is concluded that the presence of these constituents in the solvent exerts an influence which materially affects the quantity of ether extract. Therefore, it was deemed advisable to study the effect of using Squibbs ether containing approximately 3 per cent of alcohol as compared with absolute ether. In 16 of the samples analyzed the increase in extract obtained with Squibbs ether varied from 0.03 to 2.99 with an average increase of 0.57 per cent. In one sample no change was observed. In six of the samples the results showed a decrease in the quantity of extract obtained with ether containing alcohol, varying from 0.02 to 0.21 with an average of 0.12 per cent.

TABLE 3.

Effect of moisture on the determination of fat.

SAMPLE NO.	MOISTURE	PETROLIC ETHER (9 HOURS' EXTRACTION; 3 HOURS' DRYING)			PENTANE (9 HOURS' EXTRACTION; 3 HOURS' DRYING)			ABSOLUTE ETHER, 16 HOURS' EXTRACTION; ½ HOUR'S DRYING					SQUIBBS ETHER (16 HOURS' EXTRACTION, 1½ HOURS' DRYING)	
											Undried sample			
		Undried sample	Dried sample	Undried compared with dried ±	Undried sample	Dried sample	Undried compared with dried ±	Undried sample	Dried sample (Official method)	Undried compared with dried ±	Petrolic ether 9 hours extraction, 3 hours' drying, compared with Official ±	Petroleum ether 3 hours' extraction, 3 hours' drying, compared with Official ±	Dried sample	Squibbs ether compared with Official ±
	average per cent	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent*	*per cent extract*	*per cent*
1	6.72	11.16 11.26 11.38	11.06 10.81 10.72	....	11.15 11.20	11.14 11.16	....	13.44 13.74	12.43 12.54	....	......	......	15.43 15.50	....
		11.27	10.86	+0.41	11.18	11.15	+0.03	13.59	12.48	+1.11	−1.21	−1.53	15.47	+2.99
2	6.26	6.50 6.45 6.41	6.29 6.28 6.04	....	6.00 6.23	6.08 6.10	....	6.22 6.13	6.30 6.28	....	......	......	6.44 6.30	....
		6.45	6.20	+0.25	6.12	6.09	+0.03	6.18	6.29	−0.11	+0.16	−0.22	6.37	+0.08
3	5.45	10.48 10.67 10.68	10.44 10.39 10.45	....	10.39 10.62	10.42 10.30	....	10.69 10.69	10.77 10.76	....	......	......	10.87 10.79	....
		10.61	10.43	+0.18	10.51	10.36	+0.15	10.69	10.77	−0.08	−0.16	−0.49	10.83	+0.06
4	4.89	0.68 0.66 0.68	0.49 0.52 0.53	....	0.63 0.67	0.58 0.57	....	1.04 1.16	1.09 1.19	....	......	......	1.84 1.95	....
		0.67	0.51	+0.16	0.65	0.58	+0.07	1.10	1.14	−0.04	−0.47	−0.69	1.90	+0.76
5	4.02	2.91 2.99 2.91	2.79 2.56 2.71	....	2.76 2.86	2.83 2.77	....	3.23 3.37	3.57 3.61	....	......	......	3.93 3.90	....
		2.94	2.68	+0.26	2.81	2.80	+0.01	3.30	3.59	−0.29	−0.65	−0.95	3.92	+0.33

6	4 31	2.90 2.87 2 96	2.71 2.68 2.70	....	2.95 2.70	2.79 2.94	....	3.17 3.07	3.46 3.38	....	......	......	3.16 3.24	....
		2.91	2.70	+0.21	2.83	2.87	−0.04	3.12	3.41	−0.29	−0.50	−0.80	3.20	−0.21
7	7.62	6.77 6.79 6.68	6.55 6.60 6.57	....	6.37 6.45	6.34 6.38	....	6.61 6.63	6.76 6.65	....	......	......	6.58 6.70	....
		6.75	6.57	+0.18	6.41	6.36	+0.05	6.62	6.71	−0.09	+0.04	−0.23	6.64	−0.07
8	7.67	6.88 6.83 6.66	6.56 6.53 6.48	....	6.71 6.82	6.51 6.53	....	7.12 7.04	7.10 7.17	....	......	......	7.07 7.00	....
		6.79	6.52	+0.17	6.77	6.52	+0.25	7.08	7.14	−0.06	−0.35	−0.64	7.03	−0.11
9	8.00	4.02 4.12 4.07	3.97 3.82 3.71	....	3.64 3.69	3.60 3.57	....	3.99 4.00	4.02 3.92	....	......	......	3.85 3.89	....
		4.07	3.83	+0.24	3.67	3.59	+0.08	4.00	3.97	+0.03	+0.10	−0.34	3.87	−0.10
10	7.63	9.56 9.67 9.56	9.23 9.36 9 20	....	9.17 9.25	9.01 9.21	....	9.33 9.70	9.29 9.29	....	......	......	9.30 9.35	....
		9.60	9.26	+0.34	9.21	9.11	+0.10	9.52	9.29	+0.23	+0.31	−0.10	9.32	+0.03
11	5.98	9.27 9.24 9.10	9.05 9.03 9.05	....	9.01 8.98	8.99 8.97	....	9.40 9.41	9.48 9.35	....	......	......	9.40 9.40	....
		9.20	9.04	+0.16	9.00	8.98	+0.02	9.41	9.42	−0.01	−0.22	−0.51	9.40	− 0.02
12	4.36	7.61 7.58 7.66	7.25 7.24 7.36	....	7.24 7.21	7.16 7.22	....	7.59 7.69	7.69 7.65	....	......	......	7.79 7.86	....
		7.62	7.28	+0.34	7.23	7.19	+0.04	7.63	7.67	−0.04	−0.05	−0.43	7.83	+0.16
13	6.98	3.32 3.24 3.13	2.81 2.70 2.76	....	2.97 2.88	2.58 2.58	....	4.02 3.80	4.03 4.00	....	......	......	4.29 4.20	....
		3.23	2.76	+0.47	2.93	2.58	+0.35	3.91	4.02	−0.11	−0.79	−1.28	4.25	+0.23

TABLE 3—Continued.

SAMPLE NO.	MOISTURE	PETROLIC ETHER (9 HOURS' EXTRACTION; 3 HOURS' DRYING)			PENTANE (9 HOURS' EXTRACTION; 3 HOURS' DRYING)			ABSOLUTE ETHER, 16 HOURS' EXTRACTION; ½ HOUR'S DRYING					SQUIBBS ETHER (16 HOURS' EXTRACTING 1½ HOURS' DRYING)	
											Undried sample			
		Undried sample	Dried sample	Undried compared with dried ±	Undried sample	Dried sample	Undried compared with dried ±	Undried sample	Dried sample (Official method)	Undried compared with dried ±	Petrolic ether 9 hours' extraction, 3 hours' drying, compared with Official ±	Petroleum ether 3 hours' extraction, 3 hours' drying, compared with Official ±	Dried sample	Squibbs ether compared with Official ±
	average per cent	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent*	*per cent extract*	*per cent*
14	7.72	6.20 6.17 6.21	5.22 5.25 5.23	....	5.61 5.66	5.31 5.29	....	7.08	6.52 6.44	....	......	......	6.53 6.55	....
		6.19	5.23	+0.96	5.64	5.30	+0.34	7.08	6.48	+0.60	−0.29	−0.69	6.54	+0.06
15	7.10	4.67 4.67 4.77	3.95 3.93 4.14	....	4.54 4.40	4.30 4.29	....	5.05 5.11	4.75 4.85	....	......	......	4.82 4.77	....
		4.70	4.01	+0.69	4.47	4.30	+0.17	5.08	4.80	+0.28	−0.10	−0.31	4.80	0.00
16	6.70	5.15 5.15 5.23	4.84 4.89 4.78	. . .	4.85 4.82	4.76 4.77	....	5.53 5.60	5.31 5.38	. . .	......	......	5.54 5.56	....
		5.18	4.84	+0.34	4.84	4.77	+0.07	5.57	5.35	+0.22	−0.17	−0.41	5.55	+0.20
18	7.75	8.76 8.80 8.88	8.81 8.71	....	8.35 8.28	8.31 8.04	....	8.78 8.87	8.53 8.58	....	......	......	8.47 8.27	....
		8.81	8.76	+0.05	8.32	8.18	+0.14	8.83	8.56	+0.27	+0.25	+0.04	8.37	−0.19
20	6.35	4.29 4.31 4.21	3.80 3.91 3.90	....	3.73 3.75	3.50 3.63	....	5.19 4.97	4.56 4.64	....	......	......	5.25 5.14	....
		4.27	3.87	+0.40	3.74	3.57	+0.17	5.08	4.60	+0.48	−0.33	−0.68	5.20	+0.60

21	5.94	9.48 9.31 9.30	8.76 8.78 8.93	....	9.08 8 99	9.11 8.96	....	11.57 11.54	10.25 10 28	....	......	......	13.09 13.00	....
		9.36	8.82	+0 54	9.04	9 04	+0.00	11 56	10 27	+1.29	−0.91	−1.29	13.05	+2.78
22	9.19	3.77 3.80 3.78	2.74 2.67 2.64	....	3.61 3.51	2.98 2.75	....	4.20 4.16	3.84 3.76	....	......	......	4.01 3.97	....
		3.78	2.68	+1.10	3.56	2.87	+0 69	4.18	3 80	+0.38	−0.02	−0.14	3 99	+0.19
23	5.64	3.77 3.83 3.74	1.84 1.74 1.68	....	2.05 1.95	1.70 1.76	....	4.18 4.36	3.84 3.85	....	......	......	4.20 4.21	....
		3.78	1.75	+2.03	2 00	1.73	+0.27	4 27	3.85	+0.42	−0.07	−0.40	4.20	+0.35
24	11.03	2.01 2.03 1.98	1.53 1.34 1.32	....	0.94 0.90	0.93 0.91	....	1.31 1 40	1.75 1.55	....	......	......	1.73 1.78	....
		2.01	1.40	+0.61	0.92	0.92	0.00	1.36	1.65	−0.29	+0.36	+0.16	1.76	+0.11
25	9.26	4 28 4.30 4.32	4.01 4.22 3.99	....	4.09 4.04	3 95 4.04	....	5.17 5.42	4.77 4.73	....	......	......	4 97 4.85	....
		4.30	4.07	+0.23	4 07	4.00	+0.07	5 30	4.75	+0.55	−0 45	- 0 97	4 91	+0.16

It is very evident from the results obtained, not only in this investigation but also in comparative work in connection with inspection of feeding stuffs of varied composition in this laboratory that the use of ether containing alcohol and water can not be relied upon to give absolute results. The nature of the material subjected to examination appreciably influences the solvent action of the ether as is shown in Table 3. For instance, Sample 1 composed chiefly of corn distillers' grains and Sample 21, which is corn distillers' grains with no admixture, gave an increase in amount of extract with Squibbs ether of 2.99 and 2.78 per cent, respectively. With gluten feeds increases were apparent, but with linseed and cottonseed meals either slight increases or negative results were secured. Considering the widely varying results obtained with Squibbs ether as compared with absolute ether, due not only to the presence of alcohol, but also to the nature of the material under examination we would emphasize the importance of using absolute ether by all analysts in order to secure results which are comparable.

EFFECT OF TIME OF DRYING EXTRACT.

Repeated investigations in this laboratory having shown that drying ether-extracted residues $1\frac{1}{2}$ hours at the temperature of boiling water gave constant weight, it was deemed advisable to determine the length of time necessary to dry extracts with petroleum ether to secure similar results. Two additional periods, multiples of $1\frac{1}{2}$, 3, and $4\frac{1}{2}$ hours were decided upon.

Nineteen of the undried samples with Pennsylvania petrolic ether show an average loss of 0.12 per cent from $1\frac{1}{2}$ to 3 hours, while 4 show an average increase of 0.09 per cent with a general loss for the 23 samples of 0.09 per cent. For the 3 to $4\frac{1}{2}$ hour period 14 of the samples show an average increase of 0.07 per cent and 7 a decrease of 0.04 per cent with an average increase for the 23 samples of 0.03 per cent.

The dried samples show a similar variation in that all 23 samples show an average decrease from $1\frac{1}{2}$ to 3 hours of 0.19 per cent, while from 3 to $4\frac{1}{2}$ hours 15 show an average increase of 0.09 per cent, while 7 show a decrease of 0.03, 2 show no variation, making the average increase for 23 samples 0.05 per cent.

In the pentane extraction 21 of the samples show an average loss from $1\frac{1}{2}$ to 3 hours of 0.25 per cent, while 2 show an average gain of 0.07 per cent, making the average loss for the 23 samples 0.22 per cent. Thirteen show an average loss of 0.06 per cent from 3 to $4\frac{1}{2}$ hours and 10 a gain of 0.10 per cent. Twenty of the dried samples show an average loss of 0.14 per cent and 3 a gain of 0.07 per cent from $1\frac{1}{2}$ to 3 hours, making the average net loss 0.12 per cent, while from 3 to $4\frac{1}{2}$ hours 14 samples con-

tinue to lose an average of 0.07 per cent and 9 gain 0.11 per cent. The per cent of loss in all samples, however, is such as to indicate that practical work will require not to exceed 3 hours' drying of the extract.

In all cases of drying the extract the length of time required would be materially affected by the completeness of the drying before the flask was removed from the extraction machine. It will be noted that much greater losses were shown in last year's report between 2 and 4 hours.

DISCUSSION.

The difficulty of volatilizing the petroleum ether noted in the report of 1912 was again experienced, and in no case were the analysts able to distill the entire residual petroleum ether into the Soxhlets; it was necessary to volatilize this out of the receiving flask into the open.

Strict account was kept of the amount of Pennsylvania petrolic ether and absolute ether used with a view to calculating the cost per determination with each method.

It was found that 51.9 per cent of the petrolic ether was lost and that for 24 determinations the total loss amounted to one pound, which on the basis of October 17 quotations would cost 35 cents or 1.5 cents for each determination for reagent.

In the official method the loss in ether was 40 per cent, the total loss for 24 determinations, amounting to 0.8 pound, which on the basis of October 17 quotations from stock (80 cents a pound) amounts to 64 cents or 2.7 cents for each determination, and on duty-free import ($37\frac{1}{2}$ cents per pound) to 30 cents or 1.3 cents for each determination.

CONCLUSIONS.

The work of the past three years as well as past work of the association's referees leads to the following conclusions:

(1) With very rare exceptions appreciably higher amounts of crude fat may be expected on all classes of feeding stuffs from the use of the official method than from the use of the proposed petroleum ether method.

(2) That 3 hours' extraction with petroleum ether is not sufficient to secure the total petrolic ether extract, which investigation indicates requires 9 hours' extraction to secure maximum results. This is true even with cottonseed products for which the method is recommended by the previous referee.

(3) That the presence of moisture materially affects the amount of extract by the petroleum ether method depending on the nature of the material extracted.

(4) That the extraction of the same materials with petrolic ethers from different sources does not give concordant results, that is, petrolic ethers

TABLE 4. *Effect of time of drying extract. (9 hours'*

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample					Dried sample			
		1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying
	per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*
1	6.72	11.11	11.16	11.35	+0.05	+0.19	11.08	11.06	11.12	−0.02
		11.08	11.26	11.38	+0.18	+0.12	10.94	10.81	10.97	−0.13
		11.31	11.38	11.52	+0.07	+0.14	10.94	10.72	11.26	−0.22
		11.17	11.27	11.42	+0.10	+0.15	10.99	10.86	11.12	−0.13
2	6.38	6.35	6.50	6.55	+0.15	+0.05	6.41	6.29	6.38	−0.12
		6.29	6.45	6.49	+0.16	+0.04	6.18	6.28	6.28	+0.10
		6.38	6.41	6.52	+0.03	+0.11	6.18	6.04	6.08	−0.14
		6.34	6.45	6.52	+0.11	+0.07	6.26	6.20	6.24	−0.06
3	5.45	.....	10.48	10.54	....	+0.06	....	10.44	10.36	....
		10.76	10.67	10.68	−0.09	+0.01	....	10.39	10.30	....
		10.70	10.68	10.71	−0.02	+0.03	10.53	10.45	10.41	−0.08
		10.73	10.61	10.64	−0.06	+0.03	10.53	10.43	10.36	−0.08
4	4.86	0.80	0.68	0.76	−0.12	+0.08	0.73	0.49	0.49	−0.24
		0.75	0.66	0.72	−0.09	+0.06	0.54	0.52	0.49	−0.02
		0.98	0.68	0.71	−0.30	+0.03	0.60	0.53	0.54	−0.07
		0.84	0.67	0.72	−0.17	+0.05	0.62	0.51	0.50	−0.11
5	3.98	2.95	2.91	3.07	−0.04	+0.16	3.06	2.79	2.80	−0.27
		3.05	2.99	3.07	−0.06	+0.08	2.84	2.56	2.66	−0.28
		2.99	2.91	3.01	−0.08	+0.10	2.96	2.71	2.76	−0.25
		3.00	2.94	3.05	−0.06	+0.11	2.95	2.69	2.74	−0.26
6	4.27	3.03	2.90	3.03	−0.13	+0.13	2.94	2.71	2.76	−0.23
		2.97	2.87	3.02	−0.10	+0.15	2.91	2.68	2.68	−0.23
		3.10	2.96	3.07	−0.14	+0.11	2.90	2.70	2.70	−0.20
		3.03	2.91	3.04	−0.12	+0.13	2.92	2.70	2.71	−0.22
7	7.58	6.73	6.77	6.87	+0.04	+0.10	6.65	6.55	6.48	−0.10
		6.84	6.79	6.86	−0.05	+0.07	6.54	6.60	6.51	+0.06
		6.61	6.68	6.78	+0.07	+0.10	6.54	6.57	6.54	+0.03
		6.73	6.75	6.84	+0.02	+0.09	6.58	6.57	6.51	−0.01
8	7.67	6.97	6.88	6.98	−0.09	+0.10	6.84	6.56	6.54	−0.28
		6.91	6.83	6.89	−0.08	+0.06	6.72	6.53	6.54	−0.19
		6.75	6.66	6.76	−0.09	+0.10	6.68	6.48	6.46	−0.20
		6.88	6.79	6.88	−0.09	+0.09	6.75	6.52	6.51	−0.23
9	8.00	4.18	4.02	3.94	−0.16	−0.08	4.19	3.97	4.08	−0.22
		4.19	4.12	4.08	−0.07	−0.04	4.04	3.82	3.91	−0.22
		4.16	4.07	3.98	−0.09	−0.09	3.97	3.71	3.76	−0.26
		4.18	4.07	4.00	−0.11	−0.07	4.07	3.83	3.92	−0.24
10	7.63	9.50	9.56	9.51	+0.06	−0.05	9.35	9.23	9.31	−0.12
		9.51	9.67	9.59	+0.16	−0.08	9.51	9.36	9.43	−0.15
		9.36	9.56	9.50	+0.20	−0.06	....	9.20	9.21	....
		9.46	9.60	9.53	+0.14	−0.07	9.43	9.26	9.32	−0.13

extraction at temperature of boiling water, 98°C.)

PETROLIC ETHER	PENTANE									
Dried sample	Undried sample					Dried sample				
Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying
per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*
+0.06	11.38	11.15	11.33	−0.23	+0.18	11.28	11.14	11.12	−0.14	−0.02
+0.18	11.46	11.20	11.23	−0.26	+0.03	11.31	11.16	11.21	−0.15	+0.05
+0.54										
+0.26	11.42	11.18	11.28	−0.24	+0.10	11.30	11.15	11.17	−0.15	+0.02
+0.09	6.24	6.00	5.97	−0.24	−0.03	6.00	6.08	5.96	+0.08	−0.12
....	6.45	6.23	6.23	−0.21	0.00	6.05	6.10	6.01	+0.05	−0.09
+0.04										
+0.04	6.35	6.12	6.10	−0.23	−0.02	6.03	6.09	5.99	+0.06	−0.10
−0.08	10.65	10.39	10.39	−0.26	0.00	10.46	10.42	10.16	−0.04	−0.26
−0.09	10.84	10.62	10.60	−0.22	−0.02	10.43	10.30	10.18	−0.13	−0.12
−0.04										
−0.07	10.75	10.51	10.50	−0.24	−0.01	10.45	10.36	10.17	−0.09	−0.19
0.00	0.73	0.63	0.59	−0.10	−0.04	0.71	0.58	0.52	−0.13	−0.06
−0.03	0.83	0.67	0.66	−0.16	−0.01	0.70	0.57	0.44	−0.13	−0.13
+0.01										
−0.01	0.78	0.65	0.63	−0.13	−0.02	0.71	0.58	0.48	−0.13	−0.10
+0.01	2.93	2.76	2.74	−0.17	−0.02	2.93	2.83	2.81	−0.10	−0.02
+0.10	2.95	2.86	2.85	−0.09	−0.01	2.85	2.77	2.67	−0.08	−0.10
+0.05										
+0.05	2.94	2.81	2.80	−0.13	−0.01	2.89	2.80	2.74	−0.09	−0.06
+0.05	3.14	2.95	2.94	−0.19	−0.01	2.84	2.79	2.70	−0.05	−0.09
0.00	2.87	2.70	2.66	−0.17	−0.04	3.00	2.94	2.85	−0.06	−0.09
0.00										
+0.01	3.01	2.82	2.80	−0.18	−0.02	2.92	2.87	2.78	−0.05	−0.09
−0.07	6.41	6.37	6.43	−0.04	+0.06	6.57	6.34	6.46	−0.23	+0.12
−0.09	6.42	6.45	6.51	+0.03	+0.09	6.50	6.38	6.53	−0.12	+0.15
−0.03										
−0.06	6.42	6.41	6.49	−0.01	+0.08	6.54	6.36	6.50	−0.18	+0.14
−0.02	6.92	6.71	6.70	−0.21	−0.01	6.81	6.51	6.56	−0.30	+0.05
+0.01	6.98	6.82	6.81	−0.16	−0.01	6.81	6.53	6.57	−0.28	+0.04
−0.02										
−0.01	6.95	6.77	6.76	−0.18	−0.01	6.81	6.52	6.57	−0.29	+0.05
+0.11	3.68	3.64	3.49	−0.04	−0.15	3.86	3.60	3.65	−0.26	+0.05
+0.09	3.89	3.69	3.71	−0.20	+0.02	3.77	3.57	3.61	−0.20	+0.04
+0.05										
+0.09	3.79	3.67	3.60	−0.12	−0.07	3.82	3.59	3.63	−0.23	+0.04
+0.08	9.14	9.17	9.37	+0.03	+0.20	9.14	9.01	9.37	−0.13	+0.36
+0.07	9.09	9.25	9.43	+0.16	+0.18	9.14	9.21	9.51	+0.07	+0.30
+0.01										
+0.06	9.12	9.21	9.40	+0.09	+0.19	9.14	9.11	9.44	−0.03	+0.33

TABLE 4.—Continued.

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample					Dried sample			
		1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	**Gain or loss 1½ to 3 hours' drying**
	per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	***per cent***
11	5.98	9.43	9.27	9.27	−0.16	0.00	9.48	9.05	9.14	**−0.43**
		9.22	9.24	9.23	+0.02	−0.01	....	9.03	9.03	....
		....	9.10	9.17	....	+0.07	....	9.05	9.09	....
		9.33	9.20	9.22	−0.07	+0.03	9.48	9.04	9.09	**−0.43**
12	4.36	8.08	7.61	7.68	−0.47	+0.07	....	7.25	7.25	....
		7.66	7.58	7.64	−0.08	+0.06	....	7.24	7.33	....
		7.69	7.66	7.68	−0.03	+0.02	7.46	7.36	7.55	**−0.10**
		7.81	7.62	7.67	−0.19	+0.05	7.46	7.28	7.38	**−0.10**
13	6.98	3.60	3.32	3.33	−0.28	+0.01	3.09	2.81	2.81	**−0.28**
		3.48	3.24	3.24	−0.24	0.00	3.01	2.70	2.75	**−0.31**
		3.46	3.13	3.13	−0.33	0.00	3.04	2.76	2.84	**−0.28**
		3.51	3.23	3.23	−0.28	....	3.05	2.76	2.80	**−0.29**
14	7.72	6.44	6.20	6.23	−0.24	+0.03	5.43	5.22	5.19	**−0.21**
		6.36	6.17	6.13	−0.19	−0.04	5.52	5.25	5.27	**−0.27**
		6.43	6.21	6.30	−0.22	+0.09	5.50	5.23	5.23	**−0.27**
		6.41	6.19	6.22	−0.22	+0.03	5.48	5.23	5.23	**−0.25**
15	7.10	5.04	4.67	4.65	−0.37	−0.02	4.11	3.95	3.95	**−0.16**
		4.73	4.67	4.70	−0.06	+0.03	4.22	3.93	3.91	**−0.29**
		4.76	4.77	4.70	+0.01	−0.07	4.18	4.14	4.12	**−0.04**
		4.84	4.70	4.68	−0.14	−0.02	4.17	4.01	3.99	**−0.16**
16	6.70	5.33	5.15	5.18	−0.18	+0.03	5.08	4.84	4.79	**−0.24**
		5.28	5.15	5.18	−0.13	+0.03	4.95	4.89	4.83	**−0.06**
		5.31	5.23	5.18	−0.08	−0.05	4.89	4.78	4.72	**−0.11**
		5.31	5.18	5.18	−0.13	....	4.97	4.84	4.78	**−0.13**
18	7.75	8.95	8.76	8.88	−0.19	+0.12	8.96	8.81	8.97	**−0.15**
		8.82	8.80	8.78	−0.02	−0.02	8.84	8.71	8.82	**−0.13**
		8.91	8.88	8.83	−0.03	−0.05				
		8.89	8.81	8.83	−0.08	+0.02	8.90	8.76	8.90	**−0.14**
20	6.35	4.47	4.29	4.32	−0.18	+0.03	3.91	3.80	4.04	**−0.11**
		4.40	4.31	4.40	−0.09	+0.09	4.01	3.91	4.15	**−0.10**
		4.28	4.21	4.22	−0.07	+0.01	4.00	3.90	4.04	**−0.10**
		4.38	4.27	4.31	−0.11	+0.04	3.97	3.87	4.08	**−0.10**
21	5.94	9.57	9.48	9.56	−0.09	+0.08	8.98	8.76	8.79	**−0.22**
		9.41	9.31	9.50	−0.10	+0.19	9.00	8.78	8.75	**−0.22**
		9.35	9.30	9.47	−0.05	+0.17	9.08	8.93	8.88	**−0.15**
		9.44	9.36	9.51	−0.08	+0.15	9.02	8.82	8.81	**−0.20**
22	9.19	3.86	3.77	3.77	−0.09	0.00	3.24	2.74	2.84	**−0.50**
		3.88	3.80	3.80	−0.08	0.00	2.90	2.67	2.73	**−0.23**
		3.84	3.78	3.75	−0.06	−0.03	2.91	2.64	2.70	**−0.27**
		3.86	3.78	3.77	−0.08	−0.01	3.02	2.68	2.76	**−0.34**

PETROLIC ETHER	PENTANE									
Dried sample	Undried sample					Dried sample				
Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying
per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*
+0.09	9.19	9.01	9.02	−0.18	+0.01	9.25	8.99	9.02	−0.26	+0.03
0.00	....	8.98	9.04	....	+0.06	9.24	8.97	9.01	−0.27	+0.04
+0.04										
+0.05	9.19	9.00	9.03	−0.18	+0.03	9.25	8.98	9.02	−0.27	+0.04
0.00	7.42	7.24	7.29	−0.18	+0.05	7.36	7.16	7.24	−0.20	+0.08
+0.09	7.28	7.21	7.25	−0.07	+0.04	7.31	7.22	7.39	−0.09	+0.17
+0.19										
+0.10	7.35	7.23	7.27	−0.12	+0.04	7.34	7.19	7.32	−0.15	+0.13
0.00	3.08	2.97	2.98	−0.11	+0.01	3.10	2.58	2.71	−0.52	+0.13
+0.05	3.00	3.88	2.80	−0.12	−0.08	3.14	2.58	2.76	−0.56	+0.18
+0.08										
+0.04	3.04	2.93	2.89	−0.11	−0.04	3.12	2.58	2.74	−0.54	+0.16
−0.03	6.18	5.61	5.84	−0.57	+0.23	5.45	5.31	5.22	−0.14	−0.09
+0.02	6.10	5.66	5.80	−0.44	+0.14	5.39	5.29	5.27	−0.10	−0.02
0.00										
....	6.14	5.64	5.82	−0.50	+0.18	5.42	5.30	5.25	−0.12	−0.05
0.00	4.78	4.54	4.66	−0.24	+0.12	4.42	4.30	4.21	−0.12	−0.09
−0.02	4.58	4.40	4.46	−0.18	+0.06	4.37	4.29	4.27	−0.08	−0.02
−0.02										
−0.02	4.68	4.47	4.56	−0.21	+0.09	4.40	4.30	4.24	−0.10	−0.06
−0.05	5.09	4.85	4.97	−0.24	+0.12	4.85	4.76	4.74	−0.09	−0.02
−0.06	5.12	4.82	4.98	−0.30	+0.16	4.82	4.77	4.76	−0.05	−0.01
−0.06										
−0.06	5.11	4.84	4.98	−0.27	+0.14	4.84	4.77	4.75	−0.07	−0.02
+0.16	8.64	8.35	8.46	−0.29	+0.11	8.19	8.31	8.31	+0.12	0.00
+0.11	8.57	8.28	8.36	−0.29	+0.08	7.99	8.04	8.14	+0.05	+0.10
+0.14	8.61	8.32	8.41	−0.29	+0.09	8.09	8.18	8.23	+0.09	+0.05
+0.24	4.19	3.73	3.64	−0.46	−0.09	3.59	3.50	3.43	−0.09	−0.07
+0.24	4.14	3.75	3.63	−0.39	−0.12	3.70	3.63	3.54	−0.07	−0.09
+0.14										
+0.21	4.17	3.74	3.64	−0.43	−0.10	3.65	3.57	3.49	−0.08	−0.08
+0.03	9.53	9.08	9.06	−0.45	−0.02	9.07	9.11	9.11	+0.04	0.00
−0.03	9.38	8.99	8.97	−0.39	−0.02	8.91	8.96	8.90	+0.05	−0.06
−0.05										
−0.01	9.46	9.04	9.02	−0.42	−0.02	8.99	9.04	9.01	+0.05	−0.03
+0.10	3.94	3.61	3.38	−0.33	−0.23	3.01	2.98	2.95	−0.03	−0.03
+0.06	3.91	3.51	3.38	−0.40	−0.13	2.79	2.75	2.71	−0.04	−0.04
+0.06										
+0.08	3.93	3.56	3.38	−0.37	−0.18	2.90	2.87	2.83	−0.03	−0.04

TABLE 4—Continued.

SAMPLE NO.	MOISTURE	PETROLIC ETHER								
		Undried sample					Dried sample			
		1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying	1½ hour's drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying
	per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*
23	5.64	3.92	3.77	3.75	−0.15	−0.02	2.08	1.84	1.86	−0.24
		3.96	3.83	3.81	−0.13	−0.02	1.96	1.74	1.75	−0.22
		3.88	3.74	3.72	−0.14	−0.02	1.91	1.68	1.66	−0.23
		3.92	3.78	3.76	−0.14	−0.02	1.98	1.75	1.76	−0.23
24	11.03	2.14	2.01	2.00	−0.13	−0.01	1.83	1.53	1.63	−0.30
		2.18	2.03	2.01	−0.15	−0.02	1.59	1.34	1.44	−0.25
		2.10	1.98	1.97	−0.12	−0.01	1.51	1.32	1.42	−0.19
		2.14	2.01	1.99	−0.13	−0.02	1.64	1.40	1.50	−0.24
25	9.26	4.23	4.28	4.21	+0.05	−0.07	4.31	4.01	4.13	−0.30
		4.47	4.30	4.22	−0.17	−0.08	4.63	4.22	4.34	−0.41
		4.34	4.32	4.28	−0.02	−0.04	4.14	3.99	4.03	−0.15
		4.35	4.30	4.24	−0.05	−0.06	4.36	4.07	4.17	−0.29

from different crude petroleums do not give the same percentage of extract.

(5) That the extracts with petrolic ether must be dried at least 3 hours to secure constant weight.

(6) That in general the use of Squibbs ether may be expected to give higher results than the official method, although past experience well establishes the fact that this increase is not due to the presence of true glycerids of the fatty acids.

(7) That the extraction with absolute ether of samples without previous drying will in general give higher results than the official method.

In view of the results set forth in Table 3 the referee wishes to emphasize the absolute necessity of all chemists following the official method in every particular if disagreements are to be avoided.

RECOMMENDATIONS.

It is recommended that the recommendation of the referee in 1911 "That the association recognize the petroleum ether method for determining fat in cottonseed products" be not adopted for the following reasons:

(1) I do not believe the association should commit itself to the policy of recognizing special methods for individual products unless such products can not be analyzed by official methods already in use. Cottonseed

PETROLIC ETHER	PENTANE									
Dried sample	Undried sample					Dried sample				
Gain or loss 3 to 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 so 4½ hours' drying	1½ hours' drying	3 hours' drying	4½ hours' drying	Gain or loss 1½ to 3 hours' drying	Gain or loss 3 to 4½ hours' drying
per cent	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*	*per cent extract*	*per cent extract*	*per cent extract*	*per cent*	*per cent*
+0.02	2.48	2.05	1.92	−0.43	−0.13	1.82	1.70	1.62	−0.12	−0.08
+0.01	2.39	1.95	1.83	−0.44	−0.12	1.84	1.76	1.69	−0.08	−0.07
−0.02										
+0.01	2.44	2.00	1.88	−0.44	−0.12	1.83	1.73	1.66	−0.10	−0.07
+0.10	1.28	0.94	0.80	−0.34	−0.14	0.97	0.93	0.87	−0.04	−0.06
+0.10	1.27	0.90	0.79	−0.37	−0.11	0.96	0.91	0.83	−0.05	−0.08
+0.10										
+0.10	1.28	0.92	0.80	−0.36	−0.12	0.97	0.92	0.85	−0.05	−0.07
+0.12	4.03	4.09	4.14	+0.06	+0.05	3.98	3.95	3.92	−0.03	−0.03
+0.12	4.01	4.04	4.02	+0.03	−0.02	4.10	4.04	3.99	−0.06	−0.05
+0.04										
+0.10	4.02	4.07	4.08	+0.05	+0.01	4.04	4.00	3.96	−0.04	−0.04

products are not of such a nature as to preclude determination of the crude fat by the present official method.

(2) The time of extraction proposed for the petroleum ether method does not give maximum results and when the extraction and time of drying the extract is extended to accomplish this result, very little if any time is saved. In addition the question of time and cost should not be the controlling factors in official work.

(3) The comments of analysts last year indicate that much greater difficulty was experienced in securing constant extraction with petroleum ether than with ethyl ether and the experience of the referee and his assistants has been that as extraction proceeds it is necessary to add fresh petroleum ether to secure continuous action of the solvent.

(4) Results reported show that the presence of moisture in the sample has a decided influence on the amount of extract obtained from different feeding stuffs and that to some extent at least it affects the determination in cottonseed products. Hence to obtain accurate results drying the sample in hydrogen before extraction seems necessary.

(5) Petrolic ether is not of definite or stable composition and results of two analysts on the same sample may be widely at variance owing to the use of petrolic ethers from different sources. This fact is especially important at this time owing to the large demand for gasoline and similar petroleum products.

(6) The difference in cost between the two methods on the basis of the cost of solvents is a negligible quantity.

(7) The recognition of the petroleum ether method by the association would make official two methods which do not give concordant results and would lead to endless disagreements. If petrolic ether is substituted for ethyl ether as the solvent, comparison with past results will be impossible since the latter has been used almost exclusively for fat determinations in the past.

The referee desires to express his appreciation to F. D. Fuller for assistance and advice in preparing this report, and to R. E. Nelson, C. Cutler, and J. H. Roop for analytical results.

REPORT ON SUGAR AND MOLASSES.

By W. E. Cross, *Referee.*[1]

The coöperative work on sugar and molasses methods was planned along the lines suggested by previous work. The method involving the use of the Abbé refractometer has already been admitted as a provisional method for molasses, and it was considered desirable to continue the investigations to ascertain whether the methods of determining the water content of sugars with this instrument were reliable, and, furthermore, to determine whether the immersion refractometer could be satisfactorily applied to the determination of moisture in sugar products. The plan also included a comparison of the new direct polarimetric method for molasses with the official Clerget method.

Three samples, a raw sugar, a centrifugal molasses, and a blackstrap molasses, were sent to twelve prospective coöperators, but many of these found the pressure of other work too great to allow them to contribute to this work.

The following instructions accompanied the samples:

INSTRUCTIONS FOR COOPERATIVE WORK.

MOISTURE IN SUGAR (1 SAMPLE).

(1) Determine moisture in the sugar sample by the official method (Bur. Chem. Bul. 107, Rev., p. 64).

(2) Determine moisture in the sugar sample by following method: Weigh 20 grams of the sugar into a tared flask, and add about 20 grams of water. (An ordinary 100 cc. sugar flask with narrow neck is suitable.) Then stopper the flask to prevent evaporation, and dissolve the sugar completely by shaking. The total solids value of the solution is obtained by the Abbé refractometer, and temperature correction applied.

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[1] Presented by P. F. Trowbridge.

$$\text{Percentage of moisture in sugar} = \frac{2000 - XY}{20}$$

X = Percentage of total solids of solution.

Y = Weight of sugar and water.

3. Determine moisture in sugar by the following method: Weigh out 20 grams of the sugar, dissolve in a 100 cc. flask, and make up the solution to the mark. Read off the refractive value of this solution by means of the immersion refractometer (temperature must be constant and carefully noted). From this value the moisture content of the sugar is obtained by reference to the tables.[1]

It is desirable that the refractometric determinations on sugars should be made with extreme care, very special attention being paid to the temperatures, which must be constant and carefully noted. Small errors in temperature reading will produce serious differences in results.

MOISTURE IN MOLASSES (2 samples).

(1) Determine moisture in molasses by the official method (Bur. Chem. Bul. 107, Rev., p. 65.)

(2) Determine moisture by the immersion refractometer, using the following method. Weigh out 20 grams into a 100 cc. flask, and after dissolving make up to mark. Determine dry substance of this solution by means of the immersion refractometer. If the tables are not available, give refractometer reading and temperature.

POLARIZATION OF MOLASSES (2 samples).

Determine the true sucrose content of the samples by the official method (Bur. Chem. Bul. 107, Rev., p. 40).

Determine true sucrose content of the samples by the following direct method. Dissolve normal weight of molasses and make up to 100 cc. Transfer 50 cc. of the solution to another 100 cc. flask; add 6.3 cc. of sodium hydroxid solution (36° Baumé) and 7.5 cc. of hydrogen peroxid (30 per cent by weight, 100 per cent by volume). Careful cooling is necessary to prevent a too violent effervescence (ether from a dropping funnel can be used to advantage in preventing excessive foaming). Cooling in water or ice is helpful in moderating the somewhat vigorous reaction. After effervescence has almost stopped, immerse the flask in a bath at 55°C. for 20 minutes. Cool the liquid, make slightly acid with acetic acid, and make up to mark. After clarification with dry lead subacetate, filter and polarize the solution. The reading multiplied by 2 gives the percentage of true sucrose in the molasses.

Please report all temperatures and concentrations used.

It is desirable that the coöperative work should be carried out as soon as possible after receipt of the samples, as deterioration and fermentation are likely to take place if the samples are allowed to stand any length of time.

RESULTS OF COÖPERATIVE WORK.

MOISTURE IN SUGARS.

The object of this work was to determine to what extent the refractometric method could be applied to the analysis of sugars. The results are presented in Table 1:

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[1] *International Sugar Journal*, 1911, **13**: 90; La. Agr. Exper. Sta., Bul. 135, p. 13.

TABLE 1.

Moisture in sugars.

ANALYST	OFFICIAL METHOD	ABBÉ REFRACTOMETER	IMMERSION REFRACTOMETER
	per cent	*per cent*	*per cent*
W. E. Cross, New Orleans, La.	1.280	0.99	1.000
G. H. Hardin, New York, N. Y.	1.220	0.95	.....
C. L. Clay, New Orleans, La.	1.278	0.84	0.960
S. F. Sherwood, Washington, D. C.	[1]1.340	0.46	1.120
C. J. Hough, Washington, D. C.	1.175	0.46	1.015
Average	1.259	0.74	1.024

[1] After 14 hours, 1.42 per cent.

From the results sent in it would appear that the refractometric methods for sugar are not entirely satisfactory. It is recommended, however, that this work be tried out again, as there is no theoretical reason why the refractometer should give results which are so different from the drying values. While it may be admitted that very slight errors in reading, or in temperature connection, will produce serious errors in the values for moisture in the sugar, and furthermore that the limits of possible error with both instruments are rather wide, it is still thought that, with more experience with the methods, results in better accord with the true values might be obtained.

MOISTURE IN MOLASSES.

Unfortunately, very little coöperation was offered in this part of the work. The results obtained, however, as will be seen from Table 2, were promising, and made it desirable to continue the work in a succeeding year. This method is distinctly the quickest and most convenient for a dark molasses, so that it is important to discover whether or not accurate results can be obtained in this way.

TABLE 2.

Moisture in molasses.

ANALYST	FIRST CENTRIFUGAL MOLASSES		BLACKSTRAP MOLASSES	
	Official method	Immersion refractometer	Official method	Immersion refractometer
	per cent	*per cent*	*per cent*	*per cent*
Wm. E. Cross, New Orleans, La.	24.800	25.00	22.00	21.30
C. J. Hough, Washington, D. C.	27.035	27.50	26.10	24.75
S. F. Sherwood, Washington, D. C.	[1]25.890	27.65	[2]24.24	25.35
Average	25.900	26.71	24.11	23.80

[1] 27.10 in 14 hours.

[2] 26.22 in 14 hours.

POLARIZATION OF MOLASSES.

The results obtained with the determination of sucrose by direct polarization were gratifying, and show that the method is well deserving of urther study, especially as these results only confirm the satisfactory results obtained in the referee work of last year. The method is much quicker and simpler to operate than the Clerget determination, so that if it were proved reliable it would be of much service to the sugar chemist.

The results of the coöperative work are presented in Table 3.

TABLE 3.
Polarization of molasses.

ANALYST	FIRST CENTRIFUGAL MOLASSES				BLACKSTRAP MOLASSES			
	Official method		Direct method		Official method		Direct method	
	per cent	*solution*	*per cent*	*solution*	*per cent*	*solution*	*per cent*	*solution*
Wm. E. Cross, New Orleans, La.	43.03	$\frac{N}{2}$	43.10	$\frac{N}{2}$	29.0	$\frac{N}{8}$	27.40	$\frac{N}{4}$
H. Z. E. Perkins, New Orleans, La.	43.36	..	43.05	..	29.2	..	30.05	..
G. H. Hardin, New York, N. Y.	43.75	$\frac{N}{2}$	43.60	$\frac{N}{2}$	29.54	..	30.80	..
S. F. Sherwood, Washington, D. C.	43.57	..	42.12	..	23.64	..	27.55	..
C. J. Hough, Washington, D. C.	43.12	..	43.05	..	28.94	..	28.40	..
C. L. Clay, New Orleans, La.	41.00	..	42.44	..	[1]41.0	..	[1]42.44	..
Average	42.97		42.69		29.064	..	28.84	..

[1] Omitted from average.

RECOMMENDATIONS.

It is recommended that, (1) the refractometric methods for determining the moisture content of sugars, (2) the determination of the moisture content of molasses by means of the immersion refractometer, and (3) the direct determination of sucrose in molasses, be further studied.

REPORT ON TESTING CHEMICAL REAGENTS.

By J. B. Rather, *Referee.*

The work conducted by the referee differs somewhat from that taken up by the Committee on Testing of Chemical Reagents. The committee seems to have studied the impurities in the various reagents without regard to the probable effects of impurities on any particular determination. The referee has limited his work to a few reagents and has tested only for these impurities likely to be present which may affect the results of specific determinations, or whose effect on the results is not known.

The purity and strength of crude caustic soda, molybdic acid, commercial citric acid, and ethyl ether have been studied in regard to their suitability for the determination of nitrogen, phosphoric acid, insoluble phosphoric acid and ether extract respectively.

Since it could not be foretold what methods would be needed, it was considered best to conduct all the analytical work for this year in this laboratory, with the view of testing coöperatively next year, methods for the determination of those impurities whose nature and amount may justify it.

About ten samples each of crude caustic soda, molybdic acid, and commercial citric acid, were sent in by the following coöperators, and were examined with the results given in this report: R. C. Thompson, Fayetteville, Ark., Wm. G. Gaessler, Ames, Ia., A. E. Vinson, Tucson, Ariz., W. J. Jones, jr., Lafayette, Ind., Wm. P. Headden, Ft. Collins, Col., T. O. Smith, Durham, N. H., W. A. Withers, West Raleigh, N. C., J. T. Williard, Manhattan, Kans., Wm. Frear, State College, Pa., E. Van Alstine, Urbana, Ill., H. D. Haskins, Amherst, Mass.

CRUDE CAUSTIC SODA.

Methods for the determination of sodium hydroxid and sodium carbonate in crude caustic soda.

While the presence of a small amount of sodium carbonate is probably not objectionable in nitrogen determinations, a large amount tends to cause frothing, and for that reason it was thought desirable to find a satisfactory method for its determination. The amount of sodium hydroxid in crude caustic soda should be known because samples are likely to vary considerably in their content of this substance, and, therefore, a saturated solution, or one with an arbitrary percentage of crude caustic soda, is likely to vary greatly in its content of sodium hydroxid.

(*1*) *Quantitative determination and determination of sodium carbonate content* (*Krauch-Merck*).—Dissolve 2 grams of crude caustic soda in 200 cc. of water and titrate 20 cc. with fifth-normal hydrochloric acid in the cold, using phenolphthalein as an indicator. When the red color has disappeared, read the burette, add a drop of Methyl Orange, and titrate further until the color changes to red. Subtract the last reading from the first and multiply by 4. The result is percentage of sodium hydroxid. Multiply the last reading by 10.6; the result is percentage of sodium carbonate.

(*2*) (*Sutton*).—Place 100 cc. of the above solution in a 200 cc. flask, add 10 cc. of 10 per cent barium chlorid, heat to boiling, shake well, and let cool. Make up to volume, filter through a dry filter into a dry flask and titrate 40 cc. with fifth-normal hydrochloric acid and phenolphthalein. Multiply the reading by 4 to get percentage of sodium hydroxid. Subtract the reading from the sum of the two readings obtained in (1) and multiply the remainder by 5.3. The result is the percentage of sodium carbonate.

(3) *Determination of sodium carbonate by precipitation as barium carbonate. (Sutton).*—Dissolve 2 grams of crude caustic soda in water, add barium chlorid solution and heat to boiling. Filter and wash with hot water; dissolve the barium carbonate from the filter with 15 cc. of fifth-normal hydrochloric acid, wash well and titrate the filtrate, after boiling to expel carbon dioxid, with tenth-normal sodium hydroxid and phenolphthalein. Multiply fifth-normal acid consumed by 0.53; the product is percentage of sodium carbonate.

(4) *Determination of sodium carbonate by direct titration (Referee's modification).*—Dissolve 2 grams of crude caustic soda in water and titrate with approximately twice-normal hydrochloric acid and phenolphthalein until the color fades. Titrate another 2-gram portion, using 0.5 cc. less of the twice-normal acid. Now titrate this solution with fifth-normal hydrochloric acid until the color fades; read the burette, add 2 or 3 drops of Methyl Orange, and titrate until the color changes. The number of cubic centimeters of fifth-normal acid required to change the color of the Methyl Orange multiplied by 1.06 gives the percentage of sodium carbonate.

TABLE 1.

Determination of sodium hydroxid and sodium carbonate in crude caustic soda by different methods.

LABORATORY NO.	DESCRIPTION	SODIUM HYDROXID			SODIUM CARBONATE			
		(1) Krauch-Merck	(2) Sutton	(1) With titration solution doubled	(1) Krauch-Merck	(2) Sutton	(3) Barium chlorid	(4) Referee
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
7022	Greenbanks (98 per cent)	93.2	91.6	....	2.7	2.4	...	...
7023	do	93.4	91.8	....	2.1	2.1	6.0	2.0
7024	do	93.3	92.0	....	3.2	2.8	5.0	1.6
7025	Hercules	77.0	75.6	....	3.2	2.5	5.5	2.8
7036	Greenbanks (98 per cent)	93.0	94.4	92.2	2.7	3.5	4.5	2.3
7043	Baker and Adamson's Electrolytic (98 per cent)	91.6	92.8	....	3.2	1.6	4.4	1.3
7134	Greenbanks (98 per cent)	93.2	92.8	91.6	3.2	3.2	4.6	2.1
7137	Electrolytic (98 per cent)	91.6	91.6	91.2	3.2	3.2	4.8	2.4
7140	Henry Heil Chemical Co. Electrolytic (98 per cent)	92.4	92.4	91.8	3.2	3.2	4.4	...
7143	Greenbanks (98 per cent)	94.8	95.2	95.0	3.2	2.7	3.8	...

All of the samples except one contained more than 90 per cent of sodium hydroxid and that one (No. 7025) contained only about 75 per cent. The determinations of sodium hydroxid by Methods (1) and (2) leave much to be desired in the way of agreement. In both of these methods 0.1 cc. is equal to 0.4 per cent of sodium hydroxid, and it is evident that the error in titration could easily be more than 0.25 cc., equivalent to 1 per cent. While great accuracy is not necessary in this work, the limit of error could be cut in half by doubling the amount of sodium hydroxid solution taken for titration. This has been done in a few cases (see Column 5 in table). The results, however, do not differ materially from those by Methods (1) and (2).

Method (1) modified so as to double the amount of solution taken for titration, appears to be more convenient and equally as reliable as Method (2) and should be studied further.

Methods (1) and (2) for the determination of sodium carbonate gave discordant results, both among duplicate determinations and determinations by the different methods. This is due largely to the fact that 0.1 cc. of fifth-normal acid is equal to 0.53 per cent sodium carbonate; the error of titration could easily affect the result 1 per cent or more, and these methods are, therefore, considered too rough for even approximations. Results by Method (3) are much higher than by (1) and (2).

With Method (4) the samples of sodium hydroxid were by this time nearly exhausted and had no doubt taken up water from the air. The results may not be strictly comparable with those obtained by the other methods. The following results on No. 7023 were obtained with this method: 1.8, 1.9, 2.0 per cent. This method should be studied further.

The amount of sodium carbonate found in these samples, does not appear to be excessive, but further work is necessary before a limit to the amount allowed could be set.

Conditions affecting the determination of nitrogen in caustic soda.

(*A*) *Effect of the amount of sodium hydroxid on the apparent nitrogen.*—This work was undertaken to see if it would be desirable to determine the percentage of nitrogen directly, a large amount of the caustic soda being used. The methods used were as follows:

(1) Put 100 grams of caustic soda in a Kjeldahl flask with a little granulated zinc and distill into a receiver containing 5 cc. of fifth-normal hydrochloric acid. Titrate the excess of acid with tenth-normal ammonia and cochineal and report cubic centimeters of acid consumed.

(2) Proceed as in (1) but use 40 grams of caustic soda (this weight is contained in the volume of solution generally used in nitrogen determinations).

TABLE 2.

Effect of the amount of sodium hydroxid on apparent nitrogen.

LABORATORY NO.	FIFTH-NORMAL HYDROCHLORIC ACID CONSUMED	
	Method 1	Method 2
	cc.	*cc.*
7022	1.80	0.15
7023	0.65	0.10
7024	0.50	0.20
7025	0.40	0.05
7036	0.45	0.30
7043	0.55	0.10
7134	1.80	0.15
7137	1.05	0.20
7140	0.60	0.20
7143	0.80	0.05
Average	0.86	0.15

The acid consumed when 100 grams of caustic soda were taken, was in most cases much higher than when 40 grams were taken, averaging 0.86 cc. for the former and 0.15 cc. for the latter. This would correspond to an error in determination, when 0.7 gram is taken for analysis, of 0.344 and 0.060 per cent of nitrogen respectively. If the 0.15 cc. represented ammonia, in the cases where 40 grams of caustic soda were used, then the acid consumed by the distillate from 100 grams should be $2\frac{1}{2}$ times 0.15 or 0.38 cc. The result actually obtained, however, was 0.86, more than twice as much. It appears, therefore, that some of the caustic soda was carried over mechanically, thus causing an increase in the apparent nitrogen. The use of 100 grams of caustic soda in the determinates of nitrogen is undesirable and leads to erroneous results.

(B) Effect of the addition of sulphuric acid on the apparent nitrogen.—Since the use of 100 grams of caustic soda gave erroneous results, probably due to spitting of the alkali solution, it appeared possible that this same effect might be found when only 40 grams were used. In order to test this point and more nearly duplicate the conditions of an actual determination of nitrogen the following methods were used:

(1) Proceed as in Method (2) given under (A).

(2) Proceed as in (1), but add a solution containing 23 cc. of concentrated sulphuric acid to the soda before distillation, making sure that the solution is alkaline by means of phenolphthalein after the addition of the acid.

TABLE 3.

Effect of addition of acid (concentrated sulphuric) on apparent nitrogen.

LABORATORY NO.	40 GRAMS OF SODIUM HYDROXID	
	Method 1 (no acid)	Method 2 23 cc. of concentrated sulphuric acid
	cc. fifth-normal acid used	*cc. fifth normal acid used*
7022	0.13	0.15
7023	0.20	0.10
7024	0.15	0.20
7025	0.13	0.05
7036	0.15	0.30
7043	0.13	0.10
7134	0.20	0.15
7137	0.17	0.20
7140	0.17	0.20
7143	0.20	0.05
Average	0.16	0.15

The amount of acid consumed by the distillates in the two methods showed no wide variations and averaged practically the same, 0.16 cc. and 0.15 cc., for Methods (1) and (2) respectively. This would corre-

spond to an error in determination, when 0.7 gram of substance is taken, of 0.064 and 0.060 per cent of nitrogen.

From these results it appears that the use of sulphuric acid has no effect on the results when 40 grams of caustic soda are used; its use is therefore considered unnecessary.

(*C*) *Effect of redistillation of distillate on the apparent nitrogen.*—To test more conclusively whether the apparent nitrogen in the caustic soda was due to such causes as spitting, errors of solution and mensuration, six portions of 75 cc. each of a stock solution of caustic soda (Greenbanks), containing about 40 grams of sodium hydroxid, were distilled with a little zinc into fifth-normal hydrochloric acid after dilution with water, and the amount of acid consumed determined.

(1) Six portions of the same solution were distilled into distilled water, the distillate returned to a clean Kjeldahl flask and again distilled, without the addition of anything, into fifth-normal hydrochloric acid.

(2) The same amount of fifth-normal hydrochloric acid used in all the receivers (5 cc.) was measured out and diluted to about the same volume (400 cc.) as the usual distillate. The usual volume of cochineal solution was then added and the solution titrated against tenth-normal ammonia. The amount of ammonia required to neutralize the acid was divided by 2 and subtracted from the volume of acid taken. This correction for errors of solution, mensuration, and personal factor (depth of tint of color to which titrated, etc.) was applied to the average results.

TABLE 4.

Effect of redistillation of distillate on apparent nitrogen.

LABORATORY NO.	METHOD 1 (Distilled once)	METHOD 2 (Redistilled distillate)
	cc. fifth-normal acid used	*cc. fifth-normal acid used*
1	0.30	0.40
2	0.45	0.40
3	0.55	0.30
4	0.45	....
5	0.55	....
6	0.45	0.50
Average	0.46	0.40

Corrected for errors of solution, etc. (0.20 cc.), Method (1), 0.26; Method (2), 0.20; error in determination when 0.7 gram is taken. Method (1), 0.104; Method (2), 0.080 per cent of nitrogen.

The average amount of acid consumed by the solution which was distilled once (1) was 0.26 cc. (corrected), while that consumed by the redistilled product (2) was 0.20 cc. This would correspond to an error of 0.104 and 0.080 per cent nitrogen respectively when 0.7 gram is taken for analysis. The differences are small and well within the limit of error. The point, however, deserves further study. It will be noted that the cor-

rection applied was −0.20 cc., that is, the tenth-normal ammonium hydroxid required to neutralize 5 cc. of fifth-normal hydrochloric acid was only 9.80 cc. instead of 10 cc. as required by theory. This large difference was not found in our previous work. The average of a number of tests by two analysts gave the figure, −0.03.

MOLYBDIC ACID.

Methods for the determination of molybdic anhydrid.

The lead molybdate method recommended by Krauch-Merck was used first, but this proved very tedious and a slight modification made by the referee was used. Attempts were made to devise a suitable volumetric method for the determination of molybdic anhydrid. It was found that comparable results could not be obtained in a volumetric determination in the presence of the necessary excess of phosphoric acid, unless the conditions as to acidity were exactly the same. Ammonium nitrate solution was accordingly used instead of nitric acid and ammonium hydroxid.

The methods as finally used are as follows:

(*1*) (*Krauch-Merck*).—Dissolve 0.5 gram of molybdic acid in 50 cc. of water and 1 cc. of ammonium hydroxid, heating gently. Acidulate with 5 cc. of acetic acid, dilute to 200 cc. with water, heat to boiling and add a filtered solution of 1.5 gram of crystallized lead acetate in 20 cc. of water. Boil several minutes, stirring constantly. Collect the precipitate on a filter dried at 100°C. and wash with boiling water. Dry the precipitate to constant weight at 100°C. and ignite a portion. $PbMoO_4 \times 0.39247$ = Percentage of MoO_3.

(*2*) (*Referee's modification of* (*1*).—Dissolve 0.5 gram of molybdic acid in 50 cc. of water and 1 cc. of ammonium hydroxid, heating gently; filter if necessary; acidulate with 5 cc. of acetic acid, dilute to 200 cc. with water, heat to boiling, and add a filtered solution of 1.5 gram of crystallized lead acetate in 20 cc. of water. Boil several minutes, stirring constantly. Allow to settle a minute or two and decant through a Gooch crucible with a fairly thick felt, which has previously been ignited and weighed. Wash by decantation 10 times with 50 cc. portions of boiling water, allowing about a minute for the precipitate to settle each time. Transfer the precipitate to the Gooch and remove the water by suction. Ignite the precipitate with a blast lamp without further drying, cool, and weigh. The ignited precipitate is $Pb\ MoO_4$.

$$Pb\ MoO_4 \times 78.494 = \text{Percentage of } MoO_3.$$

(*3*) (*Referee*).—Dissolve 10 grams of molybdic acid in 15 cc. of ammonium hydroxid and 27 cc. of water and pour into 55 cc. of nitric acid and 100 cc. of water in a 200 cc. flask slowly and with constant shaking. Cool and make up to volume with water. Allow to settle overnight and filter. Add a solution containing 0.040 gram of P_2O_5 (sodium phosphate) to 75 cc. of water in a beaker, and add a solution containing 7.5 grams of ammonium nitrate. Heat to 65°C. and add 20 cc. of the molybdate solution. Complete as for volumetric phosphoric acid. The number of cubic centimeters of standard potassium hydroxid consumed multiplied by 2.6941 gives the percentage of MoO_3 in the molybdic acid.

TABLE 5.

Molybdic anhydrid in molybdic acid by various methods.

LABORATORY NO.	SOURCE OF SAMPLE	METHOD 1	METHOD 2	METHOD 3
		per cent	*per cent*	*per cent*
7019	In 50 pound kegs, purity unknown	85.8	85.04 85.60	.....
7020	Kalbaum's I	99.0	100.96 101.02	96.25
7021	Eimer and Amend (85 per cent)	91.7	92.20 92.23	94.36
7026	Merck, Molybdic anhydride (99.5-100 per cent)	100.5	100.05 100.53	97.26
7038	Mallinkrodt, Molybdic acid	100.4	101.44 100.48	97.65
7039	Molybdic acid (10 years old)	.....	85.79 85.45	87.90
7042	Merck, Molybdic anhydride	.....	93.55 92.64	94.29
7135	Marquard, Molybdic acid c. p.	.....	75.16 75.25	78.07
7138	Molybdic acid (85 per cent)	.....	85.59 85.58	88.30
7141	Merck, Molybdic acid	.....	90.70 90.84	92.89
7144	B. & A. Molybdic acid, c. p. (99.9 per cent)	.....	100.67 100.93	97.33

The results by the Krauch-Merck method (1) do not differ greatly from those by the method as modified by the referee; (2) the only difference in the methods is in manipulation. The original method requires practically 2 days to complete a determination, while a single determination by the modified method can be completed with good suction in 2 hours, and six determinations have been completed in 3 hours. The results by the volumetric method, (3), vary from 4.8 per cent below to 1.2 per cent above the average results of Method (2). In no case are they the same. The factor 2.6941 used in calculating these results was obtained by dividing the average of the results by Method (2) by the average of three closely-checking determinations of standard potassium hydroxid consumed by the phosphomolybdate precipitate, and using the average of the figures thus obtained. It is evident that, if there is any constant relationship between the potassium hydroxid consumed by the molybdate precipitate under the conditions, and the content of molybdic anhydrid in the molybdic acid, results obtained by the use of the factor would at least approximate those by Method (2). This is not the case; the results are invariably low when the samples are high in molybdic anhydrid and high when they are low in it. The volumetric method (3) can not, therefore, be used as a reliable method for the determination of molybdic anhydrid in molybdic acid. Method

(2), the modified Krauch-Merck method, is more rapid than either of the other two, gives closely-checking results and seems to be the most desirable of the three.

It will be noted that by Method (2) some of the samples of molybdic acid contain over 100 per cent of molybdic anhydrid. These samples were described as molybdic anhydrid (MoO_3), and all had a bluish tint due to the presence of other oxids of molybdenum (Krauch-Merck, p. 18). These oxids, MoO_2 and Mo_2O_3, contain more molybdenum than MoO_3, and this probably accounts for the higher results. Molybdic acid, H_2MoO_4, contains about 88.9 per cent MoO_3, and $H_2MoO_4{\cdot}H_2O$ contains about 80.0 per cent. The ordinary 85 per cent molybdic acid is probably a mixture of these two compounds, but the content of sample No. 7135, which is described as molybdic acid c. p. is 75.16 per cent of MoO_3. This figure is too low to be accounted for by this hypothesis.

The samples examined varied from 75.16 per cent to over 100 per cent of molybdic anhydrid. Sample No. 7021, claimed to be 85 per cent molybdic anhydrid, contained 92.2 per cent, while Sample 7042, claimed to be molybdic anhydrid, contained only 93.1 per cent of molybdic anhydrid. Molybdate solutions prepared by the official method from 7144 would have a precipitating power 33 per cent greater than 7135. In the official methods H_2MoO_4 (85 per cent) is probably meant by "molybdic acid," but nearly half of the coöperators seem to be using the anhydrid, MoO_3.

PHOSPHORIC ACID IN MOLYBDIC ACID.

Total phosphoric acid, phosphoric acid in the official molybdate solution, and sulphates were determined. The methods follow:

(*1*) *Total phosphoric acid.*—Dissolve 1 gram of molybdic acid in a few cubic centimeters of ammonium hydroxid, dilute to about 75 cc. and acidify with nitric acid. Heat at 65°C. for 15 minutes and complete as for volumetric phosphoric acid.

(*2*) *Error in phosphoric acid determinations caused by phosphoric acid in molybdate.* Prepare the solution as described in (3) under Methods for the Determination of Molybdic Anhydrid. Dilute 50 cc. with about 25 cc. of water, digest and complete as for volumetric phosphoric acid. Calculate to phosphoric acid on the basis of 0.2 gram taken for analysis.

(*3*) *Sulphates in molybdic acid.*—Dissolve 1 gram of molybdic acid in 2 cc. of ammonium hydroxid, heating gently, dilute to 150 cc. and acidify with hydrochloric acid, and heat to boiling. Add barium chlorid solution and allow the precipitate to settle. Filter and complete as usual.

TABLE 6.

Phosphoric acid and sulphates in molybdic acid.

LABORATORY NO.	METHOD (1), TOTAL PHOSPHORIC ACID	METHOD (2)[1] ERROR IN PHOSPHORIC ACID DETERMINATIONS	METHOD (3)[1] SULPHATES
	per cent	*per cent*	
7019	0.00	None	None
7020	0.00	None	None
7021	0.00	None	None
7026	0.00	None	None
7038	0.00	None	None
7039	0.00	0.08	None
7042	0.00	0.04	None
7135	0.00	0.04	None
7138	0.01	0.01	None
7141	0.00	0.04	None
7144	0.01	0.05	None

[1] No visible precipitate formed in any case, those marked "None" were not completed.

Only two samples of molybdic acid contained an appreciable amount of phosphoric acid and these only 0.01 per cent. In the determinations of phosphoric acid in the official molybdate solution no visible precipitation formed in any case and a number of the determinations were not carried further. The figures given under Method (2) represent merely errors of titration. The presence of sulphates was considered because of their probable effect on the determination of molybdic anhydrid by the lead method. No visible precipitates formed, and the determinations were not completed.

It appears that the errors introduced by phosphoric acid in molybdic acid are insignificant. The question of the effect of sulphates on the determination of molybdic anhydrid in molybdic acid should be studied further.

CITRIC ACID.

The samples of citric acid were tested for ash and oxalic, tartaric, and sulphuric acids, and sugars. The following methods were used:

Methods.

Total sugars in citric acid.—Dissolve 10 grams of citric acid in 25 cc. of water and add 5 cc. of concentrated hydrochloric acid. Heat in a water bath to 69°C. in about 3 minutes and maintain at this temperature about 7 minutes, making a total heating of 10 minutes. Remove from bath, cool rapidly to room temperature, neutralize with sodium carbonate, determine reducing sugars by Allihn's method, and determine the reduced cuprous oxid by Low's volumetric method.

Oxalic and tartaric acids.—Dissolve 10 grams of citric acid in 20 cc. of water and add 5 cc. of 1 to 2 potassium acetate solution and 50 cc. of 85 per cent alcohol. No turbidity should be produced, nor should a crystalline form appear within 2 hours.

Tartaric acid and sugar (qualitative).—Grind 1 gram of citric acid and 10 cc. of sulphuric acid together in a porcelain mortar previously rinsed with sulphuric acid.

When this mixture is heated in a test tube for an hour in a boiling water bath, it acquires at most a slight yellow color, but no brown color should develop.

Ash.—Ignite 10 grams in a tared porcelain crucible and weigh.

Sulphuric acid.—Dissolve 10 grams in water and acidify with hydrochloric acid. Add barium chlorid and complete in the usual manner.

Oxalic acid.—Neutralize a solution containing 10 grams of citric acid with ammonium hydroxid and acidify strongly with acetic acid. Add calcium chlorid and let stand a few hours, filter and wash. Ignite the precipitate and weigh. Calculate the amount of the oxalic acid present from the weight of the lime precipitate. It should be remembered that calcium citrate precipitates from the above solution when it is only weakly acid, when heated, or when it stands overnight.

Tartaric acid (qualitative).—Dissolve 0.5 gram of the sample in 10 cc. of water and add, drop by drop, to 15 cc. of lime water. No turbidity should be produced.

In the samples examined, the ash contents varied from 0 to 0.05 per cent and averaged 0.02 per cent. The amount of ash constituents introduced into 100 cc. of citrate solution would vary from 0 to 0.0093 grams. The weight 0.0093 is negligible when the relative amounts of soluble bases brought into solution by the citrate are considered, and for that reason no further examination of the ash was made.

No oxalic acid was found in the samples examined. The amount of total sugar, calculated as dextrose, varied from 0 to 0.029 per cent and averaged 0.005 per cent. All but two of the results for sugar are, however, within the limit of error. The maximum amount of sugar introduced into 100 cc. of citrate solution by the citric acid examined would be 0.0056 gram. While the effect of sugar is not known to the referee, the above amount is considered too small to justify an investigation.

In only one sample, No. 7139, was there any appreciable amount of sulphuric acid. The percentage was 0.014 and would correspond to 0.0026 gram in 100 cc. of citrate solution. Much more of the sulphates than this would quite likely be dissolved from the fertilizer sample by the ammonium citrate solution.

Qualitative tests for oxalic and tartaric acids, and for tartaric acid, gave negative results in all cases. In the test for tartaric acid and sugar a few samples gave a faint test, but this could be due to small fragments of insoluble organic matter like excelsior or paper, which are possible accidental contaminants.

In view of the results presented above, it appears that the purity of the samples of citric acid examined is as high as could be expected, and quite sufficient for fertilizer control work. The subject should be studied further.

ETHYL ETHER.

Four samples of ethyl ether, distilled over sodium (Kalbaum's) were examined for matter nonvolatile at 100°C. The method was as follows:

Method.

Evaporate 100 cc. in a tared platinum dish to dryness on a steam bath. Dry at 100°C. to constant weight.

The acidity and ash were determined in the one sample which was found to be badly contaminated. The results are shown in Table 8.

TABLE 7.

Examination of commercial citric acid.

LABORATORY NO.	SOURCE OF SAMPLE	ASH	OXALIC ACID	TOTAL SUGAR AS DEXTROSE	SULPHURIC ACID (SO_3)	QUALITATIVE TEST		
						Oxalic and tartaric acid	Tartaric acid and sugar	Tartaric acid
		per cent		*per cent*	*per cent*			
7015	Mallinkrodt	0.04	none	0.000	trace[1]	none	trace	none
7016	Bought in kegs, unknown purity	0.00	none	0.000	none	none	trace	none
7017	Eimer and Amend	0.01	none	0.005	none	none	trace	none
7018	do	0.01	none	0.000	none	none	trace	none
7037	Eimer and Amend (U. S. P.)	0.05	none	0.029	trace[1]	none	trace	none
7040	10 years old	0.01	none	0.003	trace[1]	none	none	none
7041	Baker and Adamson	0.02	none	0.003	trace[1]	none	none	none
7136	Pfitzer (99 per cent)	0.02	none	0.003	trace[1]	none	none	none
7139	Eimer and Amend	0.03	none	0.001	0.014	none	none	none
7142	Sargent and Co	0.01	none	0.001	trace[1]	none	none	none

[1] About 0.001 per cent.

TABLE 8.

Amount of various impurities in ethyl ether distilled over sodium.

SAMPLE NO.	SOURCE OF SAMPLE	NONVOLATILE AT 100 CC.	ASH	ACIDITY AS SULPHURIC ACID	ERROR IN DETERMINATION
		gram in 100 cc.	*gram in 100 cc.*	*gram in 100 cc.*	*gram in 100 cc.*
1	Kalbaum's	0.0600	0.0070	0.37	0.60 to 1.50
2	do	0.0015	......	....	0.02 to 0.04
3	do	0.0026	......	....	0.03 to 0.07
4	do	0.0022	......	....	0.02 to 0.06

The matter nonvolatile at 100°C. varied from 0.0015 gram to 0.0600 gram per 100 cc. One sample contained 0.0070 gram of ash in 100 cc. and an acidity corresponding to 0.37 per cent of sulphuric acid. The ether-blackened feed samples on which fat determinations were made and the ether residue gave off whitish fumes on ignition. In this laboratory from 20 cc. to 50 cc. of ether are taken for a determination of fat and the error introduced by the matter nonvolatile at 100°C. would vary from 0.02 to 0.07 per cent to 0.60 to 1.50 per cent. The lower figures are of slight significance, but the higher ones deserve serious attention. The method for the determination of ether impurities nonvolatile at 100°C. should be studied further, together with the question of the presence of alcohol and water, and possibly other impurities.

RECOMMENDATIONS.

It is recommended—

(1) That the lead molybdate method recommended by Krauch-Merck for the determination of molybdic anhydrid in molybdic acid, as modified by the referee, be studied coöperatively, together with the methods for the determination of nitrogen in sodium hydroxid and impurities of ether nonvolatile at 100°C.

(2) That the effect of the presence of sulphates on the accuracy of the lead molybdate method for the determination of molybdic anhydrid be studied, and that the nature and amount of the impurities in citric acid and ether, methods for the determination of sodium hydroxid and sodium carbonate in crude caustic soda, and the amount of phosphoric acid in molybdic acid, be studied further.

REPORT ON TANNIN.

By C. B. Bacon, *Referee.*

Since there has been no collaborative work on tannin analysis this past year, and, therefore, no report, it might be well worth while to call the attention of the members of the association to the more recent changes in the methods of analysis of the American Leather Chemists Association, which is composed of approximately 125 active members, who are vitally interested in the matter of tannin analysis. The points wherein their methods differ from those of the Association of Official Agricultural Chemists are briefly as follows:

1. Extraction.—In extraction the tendency is toward narrowing the permissible limits of tannin content from 0.35 to 0.45, as it now is in the Association of Official Agricultural Chemists method, to 0.375 to 0.425 grams per 100 cc.

2. Cooling.—The American Leather Chemists Association permits the rapid cooling of the solution to analytical temperature of 20°C.

3. Filtration.—The temperature of filtration is kept at 20°C.

4. Evaporation and drying.—The use of the combined evaporator and dryer is specified and the time recommended as 16 hours.

Aside from these points the methods are practically identical.

Inasmuch as extracts which contain wood pulp liquor are presented for analysis according to the official methods, it would seem advisable that the better known qualitative methods for the detection of wood pulp liquor be included so as to be available for use. Probably the best known is the modification of the lignin test by Procter and Hirst,[1] which is as follows:

[1] *J. S. C. I.* 1909, **28**: 293.

To 5 cc. of the extract solution, which should be of about the ordinary strength employed for analysis, 0.5 cc. of fresh, pure aniline is added, and the whole is well shaken, and 2 cc. of concentrated hydrochloric acid is then added to the mixture. With all ordinary extracts this has the effect of immediately clearing the turbidity caused by the aniline, and a perfectly transparent solution results, but where pine wood extract is present, even in comparatively small quantity, a precipitate is produced which gradually rises to the top of the liquid. Heating is not necessary, and on the whole not desirable, though it sometimes increases the rapidity of the separation of the precipitate. The reaction, however, is immediate, and any slight turbidity which arises after considerable standing should be disregarded, as it sometimes occurs in the case of unmixed extracts, probably from minute traces of ligneous matter.

A more recent method by Hayes[1] is as follows:

A mixture is made of 40 cc. of a 2 per cent gelatin solution and 30 cc. of glacial acetic acid. Seven cc. of the reagent is added to 10 cc. of the solution to be tested, this latter being of regular analytical strength. If wood pulp liquor is present, a precipitate is formed which persists even on heating.

Should the presence of wood pulp liquor be shown by these tests, an approximately quantitative determination may be made, if it is in considerable quantity, by using a modification of the Loewenthal method, as described by Procter.[2]

A modification of a method by Hinrichsen for the determination of tannin and gallic acid in inks has been found useful in the Bureau of Chemistry. The procedure is as follows:

Place 10 grams of ink in a 100 cc. separatory funnel, add 10 cc. of 20 to 25 per cent hydrochloric acid; shake five times with 25 cc. portions of acetic ether. Unite the acetic ether shakings in a 200 to 250 cc. separatory funnel and shake with 10 cc. portions of half saturated potassium chlorid solution until the aqueous layer does not give a reaction for iron. Evaporate the acetic ether solution of the tannin and gallic acid to dryness, preferably in vacuo, or at the lowest possible temperature. Wash the residue by means of a small amount of water into a weighed evaporating dish and evaporate to dryness on the steam bath. Dry the residue at 105°C. for 2 hours and weigh as tannin and gallic acids.

It is suggested that in the near future the methods of the Association of Official Agricultural Chemists be tested to show whether they are superior to those of the American Leather Chemists Association in order to get an even closer agreement between the two methods, so that all may profit by the collaborative work that is being done by that association.

The secretary announced that invitations had been received from a number of associations and organizations in St. Louis, for this association to meet in St. Louis in 1914 and from San Francisco for this association to meet in San Francisco in 1915. The secretary was requested and author-

[1] *J. A. L. C. A.* 1913, **8**: 79.
[2] *J. S. C. I.* 1909, **28**: 294.

ized to decline the former, expressing the appreciation of the association, and to reply to the latter that it would receive careful consideration at the next meeting.

L. F. Kebler announced a meeting of the local branch of the American Pharmaceutical Association that evening and invited all members and visitors at the convention to attend.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By P. F. Trowbridge, *Acting Chairman.*

(Dairy products, foods and feeding stuffs, sugar, water in foods, organic and inorganic phosphorus in foods, separation of nitrogenous bodies, testing chemical reagents, tannin, medicinal plants and drugs.)

DAIRY PRODUCTS.

It is recommended—

(1) That in view of the distinct advantages of the copper sulphate method of preparing milk serum, chief of which are the rapidity with which the serum can be obtained and the narrower range of readings given by whole milk, the referee for the ensuing year consider this method for the purpose of having it adopted as an optional provisional method in 1914.

Approved for final action in 1914.

(2) That the referee for the ensuing year study the Harding-Parkin method for fat determination (*J. Ind. Eng. Chem.*, 1913, **5**: 131) in comparison with the present official and provisional methods.

Approved.

(3) That the subjects now under consideration be given further study.

Approved.

(4) That in Bulletin 107, Revised, page 122, after the paragraph on Cream, the following paragraph be inserted under the heading "Condensed Milk (unsweetened):" Dilute 40 grams of the homogeneous material with 60 grams of distilled water, proceed as directed under "Milk," and correct the results for dilution; and the word "Sweetened" be inserted before the word "Condensed" in the subsequent heading.

Referred to the incoming referee for a report next year.

FEEDS AND FEEDING STUFFS.

It is recommended—

(1) That the recommendation of the referee in 1911 (Cir. 90, p. 8) that the association recognize the petroleum ether method for determining fat in cottonseed products, be not adopted.

Approved.

(2) That the referee for next year study the ratio of nitrogen to protein in American feeding stuffs.

Approved.

(3) That the referee compare the various proposed methods of crude fiber determinations with the present official methods.

Approved.

SUGAR.

It is recommended—

(1) That (1) the refractometric methods for determining the moisture content of sugars, (2) the de'ermination of the moisture content of molasses by means of the immersion refractometer, and (3) the direct determination of sucrose in molasses, be further studied.

Approved.

(2) That the referee for next year study the various methods of estimating the copper in low grade sugar products.

Approved.

WATER IN FOODS.

It is recommended—

(1) That comparison of drying organic or other materials at room temperature in partial vacuum and at atmospheric pressure be continued, using phosphorus pentoxid and calcium carbid as dehydrating agents.

Approved.

(2) That there be a further comparison of the dehydrating power of sulphuric acid, phosphorus pentoxid, calcium carbid, and metallic sodium, and any other reagent that may be found, at room temperature and at atmospheric pressure.

Approved.

(3) That the advisability be considered of using a general method for moisture, consisting of 24 or 48 hours' storage over either sulphuric acid, phosphorus pentoxid, calcium carbid, or metallic sodium, at room temperature and at atmospheric pressure to be followed by the vacuum oven at 70°C. or 100°C. for a short time.

Approved.

(4) That moisture determination by the vacuum method over sulphuric acid (Bul. 122, p. 219) be made an optional official method.

Approved for final action in 1914.

(5) That the title of the referee on Water in Foods be changed to that of referee on Water in Foods and Feeding Stuffs.

Approved.

ORGANIC AND INORGANIC PHOSPHORUS IN FOODS.

It is recommended—

(1) That methods to determine the influence of heat upon organic phosphorus compounds in animal tissues, especially in tissues containing phosphoric acid, be given further study.

Approved.

(2) That in vegetable substances (a) the completeness of the extraction, (b) the effects of using much larger amounts of magnesia mixture in the precipitation, (c) the allowing of more time for the precipitation with magnesia mixture, (d) the facilitating of the filtration by the use of the centrifuge, (e) the use of mechanical means to break up the precipitate in the acid alcohol to insure the complete solution of the phosphate, be further studied.

Approved.

(3) That the title of the referee on Organic and Inorganic Phosphorus in Foods be changed to that of referee on Organic and Inorganic Phosphorus in Foods, Feeding Stuffs, and Drugs.

Approved.

SEPARATION OF NITROGENOUS BODIES (MEAT PROTEINS).

I. Meats and beef extracts.

It is recommended—

(1) That the Kjeldahl-Gunning-Arnold method for determining total nitrogen in meat and beef extract be made official.

Adopted, final action.

(2) That in Bulletin 107, Revised, page 108, 7a, Kjeldahl-Gunning-Arnold be inserted after the word Gunning, making the sentence read: "Employ either the Kjeldahl, the Gunning, or the Kjeldahl-Gunning-Arnold method." The digestion with sulphuric acid should be continued for at least 4 hours with the first two methods, and for 2 hours after the digestion has become clear with the last method.

Adopted, final action.

(3) That the following description of the Kjeldahl-Gunning-Arnold method be given in an appropriate place in Bulletin 107, Revised: "In addition to the mercury and sulphuric acid of the Kjeldahl method add 5 to 7 grams of potassium sulphate. Digest as usual but do not add any potassium permanganate at the end. Continue the digestion for 2 hours after the liquid has become clear or 1½ hours after the digest has reached the final color."

Approved.

II. Nitrogenous bodies in meats and meat products.

It is recommended—

(1) That in Bulletin 107, Revised, page 108, 7 (b), the following method for determining insoluble and soluble protein in meat be made optional: Exhaust 7 to 25 grams of the sample (depending upon the moisture content) with 330 cc. of cold (15°C.) distilled water. Make 11 successive extractions, 4 of 50 cc., 4 of 25 cc., and 3 of 10 cc. each. Dilute the extract to 500 cc. and determine the total soluble nitrogen in 50 cc. Deduct the percentage of soluble nitrogen from the percentage of total nitrogen and multiply the difference by 6.25 to obtain insoluble protein.

Adopted, final action.

(2) That in Bulletin 107, Revised, page 108, 7 (d) the proposed method for determining the coagulable protein in meats (see report of the referee) be made optional.

Approved for final action in 1914.

(3) That the Folin method for estimating creatin and creatinin in meat and beef extract be made official, the method as originally published by Folin being modified as given in the report of the referee.

Approved for final action in 1914.

TESTING CHEMICAL REAGENTS.

It is recommended—

(1) That the lead molybdate method recommended by Krauch-Merck for the determination of molybdic anhydrid in molybdic acid, as modified by the referee, be given coöperative study, together with methods for the determination of nitrogen in sodium hydroxid and impurities of ether nonvolatile at 100°C.

Approved.

(2) That the effect of the presence of sulphates on the accuracy of the lead molybdate method for the determination of molybdic anhydrid be studied, and that the nature and amount of the impurities in citric acid, methods for the determinations of sodium hydroxid and sodium carbonate in crude caustic soda, and the amount of phosphoric acid (P_2O_5) in molybdic acid, be given further study.

Approved.

TANNIN, MEDICINAL PLANTS, AND DRUGS.

No recommendations by the committee as no reports from referees were received.

REPORT OF GENERAL COMMITTEE ON RECOMMENDATIONS OF REFEREES.

By P. F. Trowbridge, *Chairman.*

The committee recommends that, after any method has been adopted on first reading as provisional or official, it shall be referred to the succeeding referee for collaborative work and report on the results of this collaboration before it can be finally adopted as provisional or official.

Approved.

The committee announces the resignation of F. W. Woll as a member of the committee on recommendations of referees and recommends the appointment of a member to take his place for the unexpired term.

Approved.

(R. E. Stallings, of Georgia, was appointed.)

REPORT OF COMMITTEE ON RESOLUTIONS.

By J. M. Bartlett, *Chairman.*

The Association of Official Agricultural Chemists cordially endorses the action of the Secretary of Agriculture in establishing a *Journal of Agricultural Research* to serve as a medium for the publication of the research work of the United States Department of Agriculture.

The association will warmly welcome the enlargement of the scope of this journal so as to include the research work of the Experiment Stations and the extension of its mailing lists so as to include the names of those now included in the mailing list of the Experiment Station Record.

Resolved, That the cordial thanks of this association be extended to W. D. Bigelow and A. W. Bitting for the bounteous hospitality extended and the cordial good will manifested on the evening of November 17 at the laboratories of the National Canners Association.

Resolved, That the Association of Official Agricultural Chemists extend to the management of the Raleigh Hotel its sincere thanks and high appreciation for the use of the Banquet Hall and for the courtesies shown the members of this association.

Resolved, That this association hereby expresses its appreciation to President Fraps for the able, impartial, and courteous manner in which he has presided over its deliberations.

The report of the committee was approved.

REPORT OF THE AUDITING COMMITTEE.

The following report by the secretary-treasurer was examined by the auditing committee and found to be correct:

REPORT OF THE SECRETARY-TREASURER FOR THE YEAR 1912 TO 1913.

During the year, W. D. Bigelow, secretary-treasurer, resigned and the undersigned was appointed in his place. Separate statements are given of receipts and expenditures made by Mr. Bigelow since the report for 1912 and before his resignation and a detailed statement of the receipts and expenditures made by me since that time.

On July 16, 1913, the date of the statement by Mr. Bigelow, 48 Federal and State organizations and one municipal organization had paid dues for 1912 to 1913. In addition to this, dues from two States for 1911 to 1912 are included in his report as they were received too late to be incorporated in the report for last year. The report of Mr. Bigelow as secretary-treasurer, showing a balance on hand, July 16, 1913, of $149.19, is attached.

Respectfully,
(Signed) C. L. ALSBERG,
Secretary-Treasurer.

Expenditures:	
July 30, 1913. 600 folders and 475 two-cent envelopes	$26.97
Additional postage	.20
November 1, 1913. 200 numbered tags	2.00
November 15, 1913. Dues returned to a municipal board of health	2.00
Total expenditures	$31.17
Receipts:	
Received from W. D. Bigelow, balance in treasury	$149.19
Dues in stamps from South Dakota Food and Drug Commission	2.00
Total receipts	$151.19
Balance November 15, 1913	$120.02

Respectfully submitted,
(Signed) C. L. ALSBERG,
Secretary-Treasurer.

Examined and found correct:
(Signed) JOHN PHILLIPS STREET,
(Signed) W. H. MCINTIRE,
(Signed) H. D. HASKINS,
Auditing Committee.

The association adjourned at 12.40 to reassemble at 2 o'clock.

WEDNESDAY—AFTERNOON SESSION.

A report on medicinal plants and drugs was read by the referee, H. A Seil, but not submitted for publication in the Proceedings.

REPORT ON SYNTHETIC PRODUCTS.

By W. O. Emery, *Associate Referee.*

During the past year interest in coöperative work on drug products has been unusually marked, in that the number of those indicating a desire to participate in the work has been much larger than in any previous year. The samples examined, bearing the numbers 13, 14 and 15, were derived from tablets purchased in the open market and alleged to have the following active constituents: 13: "Acetanilid 2 grs. Quinin sulf. 1 gr. in each tablet;" 14: "Acetphenetidin 2.5 grs. Quinin sulf. 2.5 grs. in each tablet;" 15: "Acetanilid 2 grs. Quinin sulf. 2 grs. Morph. sulf. $\frac{1}{8}$ gr. in each tablet." The tablets, the average weights of which had been previously determined, were powdered, made up into suitable samples and submitted along with the following methods of procedure to the coöperating chemists:

ESTIMATION OF ACETANILID AND QUININ SULPHATE.

The separation of these two substances is based on the fact that the bisulphate of quinin in aqueous-acid solution is practically insoluble in U. S. P. chloroform, while acetanilid under the same conditions is readily taken up by this solvent. The procedure, therefore, resolves itself into the following steps:

Ascertain the weight of 20 or more tablets, reduce them to a powder and transfer to a glass-stoppered or well-corked flask. Weigh out on a metal scoop, watch glass, or other convenient object an amount of the powdered sample equal to or a multiple of the average weight of one tablet, transfer to a separatory funnel (Squibb form), add 50 cc. of chloroform, 20 cc. of water and 10 drops of dilute sulphuric acid, sufficient at least to insure a slight excess of this reagent in the mixture. Shake for some time vigorously, allow to clear, then draw off the solvent through a small pledget of cotton and a small (5.5 cm.) dry filter into a 200 cc. Erlenmeyer. Repeat extraction twice, using the same amount of chloroform as in the first operation. Use a fresh pledget of cotton for each withdrawal of solvent, putting the moist cotton after passage of the chloroform into the filter, where with the latter it is allowed to dry spontaneously, or by placing a few moments on the cover of a steam bath. On completion of the third extraction the separation of the two ingredients

in question is practically complete, all the acetanilid being in the chloroform, while the quinin remains in the aqueous-acid solution, with traces also in both cotton and filter.

Acetanilid.—Distill the chloroform from the three extractions by the aid of gentle heat down to about 10 cc., add 10 cc. of dilute sulphuric acid (1: 10 by volume), continuing the distillation until all the solvent has passed over. Remove to a steam or vapor bath and digest for about one hour or until the liquid has evaporated to about two-thirds the original volume. Add 20 cc. of water, digest 30 minutes longer, add 10 cc. of concentrated hydrochloric acid, then titrate with a standard solution of potassium-bromid-bromate, substantially as outlined in the method for the estimation of acetanilid and caffein.

Quinin sulphate.—Wash filter and cotton used in drying the chloroform solution of acetanilid once with 5 cc. of water, allowing latter to run into the aqueous-acid solution of quinin. Add solid sodium bicarbonate (or aqueous ammonia) in slight excess, then extract with three 50 cc. portions of chloroform, washing each portion in rotation with 5 cc. of water, and passing the solvent after clearing through cotton and a dry filter, exactly as in the extraction of acetanilid. Distill the chloroform from the several extractions down to about 10 cc., then, if it seems desirable to weigh the quinin as such, transfer residue to a small tared beaker by pouring and subsequent washing with chloroform, evaporate to apparent dryness on the steam bath, heat for an hour at 125°C. in an air bath, cool, and weigh. If, as is usually the case in combinations like the one at present under examination, the weight of quinin sulphate is desired, distill the chloroformic solution of quinin to apparent dryness by means of gentle heat, dissolve residue in 3 to 5 cc. of neutral alcohol (just sufficient to prevent precipitation by the standard acid) and titrate with fiftieth-normal sulphuric acid (using two drops of methyl red solution as indicator) until the color changes to faint red. Remove to steam bath and heat until most of the alcohol has been expelled, the color of the liquid having in the meantime become yellow again. Now add sufficient acid to restore the faint red coloration, note number of cubic centimeters expended, then multiply same by 8.66, the value of 1 cc. of fiftieth-normal sulphuric acid in milligrams of quinin sulphate $(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 \cdot 7H_2O$, to get the weight of this substance in sample taken. In the event that the quinin as such has first been weighed, the weight should be further checked by titration, substantially as outlined.

Comments and suggestions.—The composition of many medicinal preparations in pill or tablet form is frequently of such a nature as to completely inhibit any rational separation of the active organic constituents by means of immiscible solvents in the ordinary separatory funnel, owing to the formation of persistent emulsions even on cautious agitation. To obviate this difficulty various flattened types of separators have been suggested by workers in the Bureau of Chemistry, one of which (illustrated in *J. Amer. Chem. Soc.*, 1913, **35**: 295) yields gratifying results. A 20-minute treatment on the rotating table suffices to effect a maximum distribution of the substances involved. Wherever available such separators will be found highly advantageous in obviating the delay and annoyance occasioned by emulsifying mixtures. Since quinin sulphate readily loses a portion of its water of crystallization when exposed to dry air, the amount of sulphate found, whether calculated from the quinin as

weighed or from that determined volumetrically, need not necessarily correspond with the declared amount of this commodity indicated on the sample under investigation. As far as the separation is concerned the method differs in no particular from that outlined for the preceding combination. In the estimation, however, the procedure as applied to acetphenetidin is materially shortened, in that the physical properties of this substance permits its being weighed directly.

Acetphenetidin.—Extract with three 50 cc. portions of chloroform, washing each portion in rotation in a second separator (Squibb form) with 5 cc. of water and passing solvent after clearing through a pledget of cotton and small dry filter into a 200 cc. Erlenmeyer. Distill the chloroform from the combined extractions down to about 10 cc., transfer residue by pouring and washing with additional chloroform to a small tared crystallizing dish, allow to evaporate spontaneously or at a moderate heat on the steam bath, cool, and weigh at intervals until the loss does not exceed 0.5 mg.

Quinin sulphate.—Follow directions as given under acetanilid and quinin sulphate.

Comments and suggestions.—In all cases where cotton is used to remove suspended moisture from chloroform as suggested in the foregoing work, the material is inserted in the outlet tube, thus intercepting most of the moisture and any suspended matter that might otherwise clog the filter.

ESTIMATION OF ACETANILID, QUININ SULPHATE AND MORPHIN SULPHATE.

As in a mixture of acetanilid and quinin sulphate, so likewise in the present combination, the alkaloidal constituents in aqueous-acid solution are separated from the third by virtue of the insolubility of their sulphates in chloroform. The separation of the alkaloids themselves is based on the ability of morphin to yield with an alkaline base a morphinate insoluble in chloroform. The procedure thus resolves itself into the following particulars:

Acetanilid.—Transfer to a separatory funnel an amount of the powdered sample equal to or a multiple of the average weight of one tablet (the amount of morphin sulphate represented should not be less than 0.25 grain), add 20 cc. of water and 10 drops of dilute sulphuric acid, then extract with three 50 cc. portions of alcohol-free chloroform, the subsequent manipulations being substantially as directed for this ingredient in the combination: Acetanilid and quinin sulphate.

Quinin sulphate.—Wash filter and cotton used in drying the chloroformic solution of acetanilid once with 5 cc. of water, uniting latter with the aqueous-acid solution of quinin and morphin. To this solution add 4 to 5 cc. of aqueous sodium hydroxid (5 grams of pure sodium hydroxid in 50 cc. of water), then extract with three 50 cc. and one 25 cc. portions of U. S. P. chloroform, transferring latter in rotation to a second separator (Squibb type) containing 5 cc. of water, wash and pass the nearly clear chloroform through a pledget of cotton and small filter into a 200 cc. Erlen-

meyer, from which the solvent is later removed by gentle distillation and the residue titrated, substantially as outlined for quinin in the combination: Acetanilid and quinin sulphate.

Morphin sulphate.—Wash filter and cotton employed in the preceding operation with 5 cc. of water, which latter together with that portion used to wash the chloroformic solution of quinin is united with the aqueous-alkaline solution of sodium morphinate. Now add 0.5 gram of ammonium chlorid (an amount slightly in excess of that required to free the morphin as well as convert the sodium hydroxid into sodium chlorid) and to the resulting ammoniacal solution add 45 cc. of U. S. P. chloroform and 5 cc. of alcohol, then extract and draw off solvent into a second separator containing 5 cc. of water, wash, allow to clear, then pass chloroform through cotton and filter into a 200 cc. Erlenmeyer. Repeat extraction and subsequent washing with one 50 cc., one 40 cc. and one 30 cc. of U. S. P. chloroform, finally collecting the solvent from all extractions in and distilling from the aforesaid Erlenmeyer down to about 10 cc. Transfer by pouring and washing with additional chloroform to a small tared beaker, evaporate on the steam bath to dryness, cool and weigh the residual morphin now appearing as a transparent varnish. To render crystalline, dissolve by warming with about 1 cc. of neutral alcohol, and about the same quantity of water drop by drop, rubbing the glass with a rod to induce crystallization, then evaporate slowly on the steam bath to dryness. Cool and weigh a second time. Check the weight of morphin thus found by titration with fiftieth-normal sulphuric acid, using a drop of methyl red solution as indicator. To this end dissolve the morphin in 1 to 2 cc. of warm neutral alcohol; then after solution is complete add the acid till the color changes to faint red. Evaporate most of the alcohol on the steam bath, and in the event that the color has reverted to yellow add just sufficient acid to restore the faint red coloration. Note volume of acid expended, then multiply the number of cubic centimeters by 7.53 (the number of milligrams of morphin sulphate equivalent to 1 cc. of fiftieth-normal sulphuric acid) to ascertain the quantity of morphin sulphate in the sample taken. The amount of anhydrous or of crystallized alkaloid can also be determined from the titration value by means of the proper factor.

Comments and suggestions.—For the purpose in question alcohol-free chloroform may be conveniently prepared by washing the pharmacopoeial product several times with water. All cotton used for drying chloroform should first be freed from fatty material of other extractives by thorough washing with this solvent, all of which latter may be regained by distillation. In the various operations involving fixation and subsequent liberation of morphin by means of fixed alkali and ammonium chlorid, strict attention should be paid to the matter of adding these reagents, since any undue excess of either might nullify the entire procedure. Any large excess of sodium hydroxid would naturally require for its reduction a correspondingly large amount of ammonium chlorid, the latter in turn yielding its prorata of ammonium hydroxid, relative large quantities of which through interaction with sodium chlorid tend to inhibit any permanent liberation of the alkaloid and thus prevent a complete extraction. Furthermore, the presence of relatively large quantities of ammonium chlorid as such operates to a partial retention of morphin in solution, due in part,

possibly, to the formation of the hydrochlorid of this alkaloid. In spite of all precautions in the matter of excluding impurities from the morphin, the amount of this substance as found by weight will usually be greater than that determined volumetrically. In order to insure greater accuracy in volumetric operations with alkaloidal substances, as quinin and morphin, the suggestion is made, in all cases where possible, that the strength of the standard acid used be checked by titration against the pure alkaloid under examination.

COÖPERATIVE RESULTS.

Coöperative results on synthetic products.

ANALYST	13[1]			14[2]			15[3]				
	ACETANILID	QUININ SULPHATE		ACETPHENETIDIN	QUININ SULPHATE		ACETANILID	QUININ SULPHATE		MORPHIN SULPHATE	
		Gravimetric	Volumetric		Gravimetric	Volumetric		Gravimetric	Volumetric	Gravimetric	Volumetric
	grains	*grains*	*grains*	*grains*	*grains*	*grains*	*grains*	*grains*	*grains*	*grains*	*grains*
L. A. Brown, Lexington, Ky.	1.90	0.98	0.97	2.51	2.47	2.38	1.92	1.94	1.89	0.109	0.093
	1.89	0.99	0.97	2.54	2.45	2.41	1.91	1.95	1.89	0.105	0.090
J. F. Darling New York, N. Y	1 96	1.01	1.02	2.51	2.54	2.47	1.93	1.86	1.82	0.184	0.162
E. O. Eaton, San Francisco, Cal.	1.92	0.98	0.87	2.47	2.10	2.01	1.90	1.87	1.72	.....	.....
	1.92	1.01	0.87	2.47	2.18	2.09	1.90	1.88	1.72	.....	.....
W. O. Emery, Washington, D. C.	1.98	....	0.96	2 49	....	2.45	1.90	....	1.91	0.080	0 068
H. Engelhardt and O. E. Winters, Baltimore, Md.	1 91	0.98	0.94	2.43	2 22	2.21	1 97	1.83	1.81	0.200	0.148
	1 98	1.04	0 95	2.56	2.42	2.36	1.94	1.86	1.79	0.208	0.151
H. C. Fuller, Washington, D. C	1.96	1.00	....	2.49	2.40	....	1.89	1.96	....	.....	0.080
F. Goodrich, Seattle, Wash[4].	2.01	....	0.96	2.43	....	2.30	2.05	....	1.90	.....	0.128
	1.91	....	0.97	2.45	....	2.39	2.08	....	1.89	.....	0.093
E. G. Grab, Nashville, Tenn.	1.98	1.01	0.93	2 49	2.42	2.35	1.93	1.94	1.93	0.138	0.078
	1.98	0.98	0.96	2.49	2.42	2.29	1.92	1.93	1.94	0.133	0.089
C. B. Morison, New Haven, Conn[5].	1.99	....	0.93	2.47	....	2.28	1.99	....	1.83	.....	0.090
E. E. Sawyer, Orono, Me.[6]	2.03	0.99	0.93	2.64	2.48	2.26	1.83	1.90	1.64	0.129	0.068
H. A. Seil, New York, N. Y.	1.98	1.00	1.00	2.44	2.53	2.44	1.90	2.02	1.88	.....	0.132
O. Stockinger, Philadelphia, Pa.[7]	1.97	0.98	0.95	2.51	2 47	2.30	1 92	....	1.94	0.043	0.033
	1.96	....	....	2.48	2.45	2.30	1.92	....	1.93	0.033	0.025
E. R. Tobey, Orono, Me.[6]	2.00	0.91	0 89	2.53	2.44	2.37	1.89	1.91	1.81	0.090	0.076
A. R. Todd, Lansing, Mich.	1.90	....	0.96	2.42	....	2.45	1.87	....	1.50	.....	0 500
C. C. Wright, Washington, D. C.	2 00	1.00	0.92	2.50	2.46	2 42	1.91	1.87	1.80	0.129	0.098
	2 00	1.01	0.95	2.50	2 47	2 39	1.90	1.88	1.79	0.125	0.101
Declared	2.00	1.00		2.50	2.50		2 00	2.00		0.125	

[1] Average weight of the single tablet, 0.2632 gram.
[2] Average weight of the single tablet, 0.3851 gram.
[3] Average weight of the single tablet, 0.2939 gram.
[4] Reported by C. W. Johnson.
[5] Reported by J. P. Street.
[6] Reported by J. M. Bartlett.
[7] Reported by C. E. Vanderkleed.

Examination of the data herein presented by 15 chemists indicates that little or no trouble was experienced in estimating acetanilid and acet-

phenetidin, the recoveries corresponding very closely with the amounts of active ingredients alleged to be present. Some of the workers appear to have had difficulty with quinin, while in the separation of this substance from morphin and the estimation of this latter constituent considerable trouble must have been experienced, as indicated by the widely-varying results, and by the comments of the workers themselves. In manipulating the several mixtures with the ordinary type of separatory funnel, more or less difficulty would necessarily be encountered owing to a tendency of the tablet excipients to favor emulsification. No. 15 in particular was undoubtedly the most difficult problem in this respect, hence it is not a little to be wondered at that some of the least experienced workers were able to effect a gross separation at all with the apparatus generally available and to arrive at the commendable results presented. Apparently one-third of the workers had never before had opportunity to examine such samples. About half those coöperating had no suggestions or criticisms to offer relative to the methods followed, from which the inference is drawn that little or no trouble was encountered by them in carrying out the various operations. Others, however, were kind enough to formulate their experience in the following terms:

COMMENTS BY COLLABORATORS.

L. A. Brown had no criticism or suggestion except as to Sample 15, in which case it was necessary to use more than one tablet in order to get a workable amount of morphin. He found 3 to 50 cc. portions of chloroform insufficient to extract all the acetanilid. Furthermore, in the titration of quinin, from a sample of three tablets used by him, the alkaloid was dissolved in 50 cc. of neutral alcohol and then aliquot portions titrated.

J. F. Darling believed the method would be improved by a provision for removal of any insoluble gum prior to extraction. His separation of quinin from morphin was not sharp, some of the former appearing with the morphin residue.

E. O. Eaton's experience with No. 15 was so unsatisfactory that no analytical returns were made on this mixture. No other criticisms reported. One would infer, however, that some difficulty had been encountered with quinin in No. 14.

H. Engelhardt and O. E. Winters found the method satisfactory except as affected by persistent emulsification in No. 15.

E. G. Grab referred in connection with the hydrolysis of acetanilid and acetphenetidin to the transfer of the 10 cc. of chloroformic residue containing one of these substances after addition of dilute sulphuric acid directly to steam bath, as being preferable to further recovery of solvent, since the last runnings of chloroform are likely to carry suspended water and thus contaminate the main portion. His point is that little is gained in attempting to recover the chloroform after addition of acid.

C. E. Vanderkleed is of the opinion that accurate determinations of morphin sulphate are scarcely possible when working on such small quantities of material as called for in the method.

The *referee* believes notwithstanding that the method will yield accurate results with an amount of morphin sulphate as small as one-fifth of a

grain, provided the directions are followed closely as to detail and emulsification is avoided by the use of the so-called "terrapin" form of separator. This belief is based on results obtained with controls.

H. A. Seil, in commenting on the titration of quinin stated that solution of the alkaloid in standard fiftieth-normal acid with subsequent titration of excess acid with fiftieth-normal alkali gives more accurate results and a sharper end point. Methyl Red as indicator appears to be better adapted to the alkaline end point than to the acid end point. In the separation of acetanilid and acetphenetidin from quinin, a wash with dilute acid in the second separatory funnel insures a cleaner separation. This method would do away with filtration through cotton plugs and would simplify the method from a mechanical standpoint. Similarly, a wash with dilute alkali in the second separatory funnel would insure a cleaner separation in the estimation of quinin from morphin.

CONCLUSION.

Taken as a whole, the results are very promising and indicate that the methods are correct in principle, requiring slight changes, if any, in the matter of detail.

A paper on the Estimation and Separation of Antipyrin from Various Synthetic Products by Means of its Periodid, by W. O. Emery and S. Palkin, was read by Mr. Palkin. It has since been published under the title: Studies in Synthetic Drug Analysis. II—Estimation of Antipyrin, in the *Journal of Industrial and Engineering Chemistry*, 1914, volume 6, page 751.

The associate referee on medicated soft drinks had no report but recommended that the following paper by Mr. St. John be read.

SUGGESTIONS ON THE ANALYSIS OF MEDICATED SOFT DRINKS.

By B. H. St. John.

SALICYLIC ACID, BENZOIC ACID, AND SACCHARIN.

Some work has been done toward finding a satisfactory method for the separation and accurate determination of salicylic and benzoic acids and saccharin, and as a result of this work the following method has been evolved which will permit also the determination of caffein in the sample if desired.

Method. Make 100 cc. of the sample distinctly acid with sulphuric acid and shake with 50 cc. of a mixture of 7 parts of chloroform and 3 parts of alcohol. Run the chloroform layer into a second separator and wash with a strong solution of sodium carbonate. If it is desired to determine caffein, wash the chloroform, after it has

been shaken with a sodium carbonate solution, with water in a third separator and filter off through a filter wetted with chloroform. Repeat this operation with successive portions of 50 cc. of the chloroform-alcohol mixture. It will be found that the caffein will be completely extracted and that the caffein residue obtained by evaporating this washed chloroform will be almost free from coloring matter, as a large proportion will be removed by the sodium carbonate.

The sodium carbonate solution will contain benzoic and salicylic acids and saccharin if present. The salicylic acid can be readily separated and determined by adding iodin solution in excess, warming on the steam bath for an hour or so, and filtering off the rose-colored precipitate whose composition is $(C_6H_2I_2O)_2$, drying and weighing. The weight of the precipitate times 0.4657 gives the weight of sodium salicylate present. When the filtrate is acidified and the iodin removed by hyposulphite or sulphurous acid the benzoic acid and saccharin can be shaken out with the above mixture of alcohol and chloroform.

The separation of benzoic acid and saccharin is more difficult, as under the conditions where benzoic acid is distilled with steam some saccharin will come over also. It is possible that the saccharin under proper conditions could be precipitated almost completely as silver salt, at least to such an extent that none would distill off with steam with the benzoic acid; or the benzoic acid may be sublimed off from the saccharin by being heated in an oven to constant weight, the residue being saccharin.

The saccharin can also be separated by transforming it to salicylic acid by heating with saturated solution of sodium hydroxid, and precipitating the salicylic acid with iodin as just described.

The quickest and easiest method is perhaps the sublimation method.

PHOSPHORIC ACID.

The present method for the determination of phosphoric acid requires much time for making the precipitation, which even then is not always complete in such preparations as medicated soft drinks. Furthermore, the composition of the precipitate frequently is not that of magnesium ammonium phosphate or phosphomolybdic acid, in which form it is desired that phosphoric acid be separated.

The following modification is the result of some work done in the past year on the subject, and it is desired to offer this with whatever suggestions may be made towards its improvement for cöoperative work during the following year.

Method.—Dilute the sample, usually 25 to 100 cc., with water, add 30 cc. of aqua ammonia, surround the beaker with ice, and run in slowly from a burette 50 cc. of magnesia mixture, stirring vigorously. Continue the stirring, preferably, of course, by means of a stirring machine, for a half hour, when precipitation will be found to be complete and the precipitate in the form of magnesium ammonium phosphate as desired. Filter off the precipitate and wash with a mixture of 1 volume of aqua ammonia and 3 volumes of water (which should be as cold as possible) until the washings have no appreciable color. Dissolve in as small as possible a quantity

of warm dilute nitric acid, then add about 50 to 75 cc. of ammonium molybdate solution and allow to stand 12 hours in a warm place at 50° to 60°C. This time may be materially shortened by stirring. Filter and wash with a solution containing 90 grams of ammonium nitrate and 200 cc. of nitric acid (specific gravity 1.2) per liter.

Dissolve the precipitate of phosphomolybdic acid in aqua ammonia, make up to approximately 100 cc., and then proceed as in the first precipitation of the magnesium ammonium phosphate, ignite the precipitate after filtering and washing, and weigh the magnesium pyrophosphate.

GLYCERIN.

In the determination of glycerin in medicinal soft drinks, if a sample of 10 to 25 cc. is taken, the method given in Bulletin 107, Revised, for the determination of glycerin in wines will give a quite satisfactory separation of glycerin from the sugars and gums present. Caffein and other substances are likely to be present, however, in the residue from this method, and consequently its weight does not represent glycerin alone.

It is advisable to dissolve the residue in water and oxidize the glycerin with alkaline permanganate to oxalic acid, removing the excess of permanganate with c. p. methyl alcohol. Make up solution to a suitable volume, filter, acidify an aliquot taken from the filtrate, boil off the carbon dioxid, make alkaline with ammonium hydroxid and precipitate with calcium chlorid solution. The calcium oxalate can be ignited and weighed as calcium oxid or calcium sulphate or dissolved in sulphuric acid and titrated with permanganate.

The association adjourned.

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J. D. Turner, Lexington, Ky. W. F. Hand, Agricultural College, Miss.

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Phosphoric acid: A. J. Patten, East Lansing, Mich.
Nitrogen:
- Determination: R. N. Brackett, Clemson College, S. C.
- Separation of nitrogeneous substances: A. W. Bosworth, Geneva, N. Y.

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Tannin: C. B. Bacon, Washington, D. C.
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Inorganic plant constituents: B. E. Curry, Durham, N. H.
Medicinal plants and drugs: H. A. Seil, Pittsburgh, Pa.
Water: W. W. Skinner, Washington, D. C.
Testing chemical reagents: J. B. Rather, College Station, Tex.
Water in foods and feeding stuffs: W. J. McGee, Washington, D. C.
Organic and inorganic phosphorus in foods, feeding stuffs, and drugs: E. B. Forbes, Wooster, Ohio.

Associate referees.

Phosphoric acid: L. S. Walker, Amherst, Mass.
Nitrogen:
- Determination: H. D. Haskins, Amherst, Mass.
- Special study of Kjeldahl method: I. K. Phelps, Washington, D. C.
- Separation of nitrogeneous substances:
  - Milk and cheese: Leroy S. Palmer, Columbia, Mo.
  - Vegetable proteins: T. B. Osborne, New Haven, Conn.
  - Meat proteins: A. D. Emmett, Urbana, Ill.

Potash:
Determination: T. D. Jarrell, College Park, Md.
Availability: E. E. Vanatta, Columbia, Mo.
Soils: A. W. Blair, New Brunswick, N. J.
Nitrogeneous compounds: C. B. Lipman, Berkeley, Calif.
Alkali in soils: R. F. Hare, State College, N. Mex.
Dairy products: W. M. Clark, Washington, D. C.
Feeds and feeding stuffs: A. C. Summers, Columbia, S. C.
Feed adulteration: Carlton Cutler, W. Lafayette, Ind.
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Vinegar: E. H. Goodnow, St. Paul, Minn.
Flavoring extracts: A. E. Paul, Chicago, Ill.
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Baking powder: R. E. Remington, Fargo, N. Dak.
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Tea and coffee: J. M. Bartlett, Orono, Me.
Preservatives: A. F. Seeker, New York, N. Y.
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Julius Hortvet, St. Paul, Minn.
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Recommendations of Referees and Revision of Methods.

(Figures in parenthesis refer to year in which appointment expires.)

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SUBCOMMITTEE B: R. E. Stallings (1918), P. F. Trowbridge (1916), *E. M. Chace, (1914), chairman, Bureau of Chemistry, Washington, D. C.* (Dairy products, foods and feeding stuffs, sugar, water in foods and feeding stuffs, organic and inorganic phosphorus in foods, feeding stuffs, and drugs, separation of nitrogeneous bodies, testing chemical reagents, tannin, medicinal plants and drugs.)

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Proposed Journal of Agricultural Chemistry.

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Study of Vegetable Proteins.

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Availability of Phosphoric Acid in Basic Slag.

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Review of the Analysis of Lime Sulphur Solutions.

G. A. Hulett, Princeton, N. J., *chairman.*
C. S. Cathcart, New Brunswick, N. J.
H. H. Hanson, Orono, Me.

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PROCEEDINGS OF THE THIRTY-FIRST ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1914.

FIRST DAY.

MONDAY—MORNING SESSION.

The thirty-first annual convention of the Association of Official Agricultural Chemists was called to order by the president, E. F. Ladd, of Fargo, N. D., on the morning of November 16, 1914, at the Raleigh Hotel, Washington, D. C. The following members and visitors were present:

MEMBERS AND VISITORS PRESENT.

Abbott, J. S., Bureau of Chemistry, Washington, D. C.
Adams, A. B., Bureau of Internal Revenue, Washington, D. C.
Albrech, M. C., Lutz and Schramm Co., Pittsburgh, Pa.
Albright, A. R., Bureau of Chemistry, Washington, D. C.
Alsberg, C. L., Bureau of Chemistry, Washington, D. C.
Ames, J. W., Agricultural Experiment Station, Wooster, Ohio.
Anderson, F. T., Bureau of Chemistry, Washington, D. C.
Andrews, J. P., Office of Experiment Stations, Washington, D. C.
Appleman, C. O., Agricultural Experiment Station, College Park, Md.

Babcock, J. H., Office of Experiment Stations, Washington, D. C.
Bailey, C. H., University Farm, St. Paul, Minn.
Bailey, E. M., Agricultural Experiment Station, New Haven, Conn.
Bailey, H. S., Bureau of Chemistry, Washington, D. C.
Bailey, L. H., Bureau of Chemistry, Washington, D. C.
Baker, E. L., Patent Cereals Co., Geneva, N. Y.
Baker, H. A., 447 West Fourteenth Street, New York, N. Y.
Balcom, R. W., Bureau of Chemistry, Washington, D. C.
Baldwin, H. B., Department of Health, 927 Broad Street, Newark, N. J.
Balls, A. K., Bureau of Chemistry, Washington, D. C.
Bartlett, G. M., Jos. Campbell Co., Camden, N. J.
Baston, G. H., Bureau of Plant Industry, Washington, D. C.
Bates, Carleton, Bureau of Chemistry, Washington, D. C.
Baughman, W. F., Bureau of Chemistry, Washington, D. C.
Beal, W. H., Office of Experiment Stations, Washington, D. C.
Beattie, J. H., Bureau of Soils, Washington, D. C.
Bengis, Robert, Bureau of Chemistry, Washington, D. C.
Beyer, G. F., Bureau of Internal Revenue, Washington, D. C.

Bidwell, G. L., Bureau of Chemistry, Washington, D. C.
Bigelow, W. D., National Canners Association, Washington, D. C.
Bishop, H. E., State Board of Health, Indianapolis, Ind.
Black, O. F., Bureau of Plant Industry, Washington, D. C.
Bonney, V. B., Bureau of Chemistry, Washington, D. C.
Bornmann, J. H., Bureau of Chemistry, Washington, D. C.
Boyett, W. L., State Food Inspector, College Station, Tex.
Boyle, Martin, Bureau of Chemistry, Washington, D. C.
Boyles, F. M., McCormick and Co., Baltimore, Md.
Brackett, R. N., State Chemist, Clemson College, S. C.
Bradbury, C. M., State Department of Agriculture, Richmond, Va.
Breckenridge, J. E., American Agricultural Chemical Co., 2 Rector Street, New York, N. Y.
Brewster, J. F., Bureau of Chemistry, Washington, D. C.
Briggs, L. J., Bureau of Plant Industry, Washington, D. C.
Brinton, C. S., Food and Drug Inspection Laboratory, U. S. Appraiser's Stores, Philadelphia, Pa.
Brinton, Mrs. C. S., Haddonfield, N. J.
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Browne, C. A., 80 South Street, New York, N. Y.
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Bunzel, H. H., Bureau of Plant Industry, Washington, D. C.
Burnet, W. C., Food and Drug Inspection Laboratory, Savannah, Ga.
Burnet, Mrs. W. C., Savannah, Ga.
Burnett, L. B., Bureau of Chemistry, Washington, D. C.

Callaway, Joseph, jr., Bureau of Chemistry, Washington, D. C.
Callenbach, J. A., Churchfield Fertilizer Co., Spartenburg, S. C.
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Cook, F. C., Bureau of Chemistry, Washington, D. C.
Coopersmith, S., Bureau of Chemistry, Washington, D. C.
Crampton, C. A., Institute of Industrial Research, Washington, D. C.
Cutler, Carleton, Agricultural Experiment Station, Lafayette, Ind.

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Dewey, G. C., National Canners Association, Washington, D. C.
Dodge, C. O., Bureau of Chemistry, Washington, D. C.

Donk, P. J., National Canners Association, Washington, D. C.
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Dunlap, F. L., Victor Chemical Works, Chicago, Ill.

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Emery, W. O., Bureau of Chemistry, Washington, D. C.
Ewing, C. O., Bureau of Chemistry, Washington, D. C.

Feldbaum, Jacob, Bureau of Chemistry, Washington, D. C.
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Griffin, E. L., Bureau of Chemistry, Washington, D. C.
Grotlisch, V. E., Bureau of Chemistry, Washington, D. C.

Hagedorn, C. F., Armour Fertilizer Works, Chicago, Ill.
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Huckle, Clarence, Bureau of Chemistry, Washington, D. C.
Hudson, C. S., Bureau of Chemistry, Washington, D. C.
Huston, H. A., 42 Broadway, New York, N. Y.

Ingle, M. J., Bureau of Chemistry, Washington, D. C.
Ingersoll, E. H., Bureau of Animal Industry, Washington, D. C.

Jackson, F. A., Food and Drug Commission, Woonsocket, R. I.
Jackson, R. F., Bureau of Standards, Washington, D. C.
Jacobs, B. R., General Baking Co., 30 Church Street, New York, N. Y.
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Johnson, J. M., Bureau of Chemistry, Washington, D. C.
Johnson, M. O., Bureau of Animal Industry, Washington, D. C.
Jones, C. H., Agricultural Experiment Station, Burlington, Vt.

Kebler, L. F., Bureau of Chemistry, Washington, D. C.
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Keister, J. T., Bureau of Chemistry, Washington, D. C.
Kellogg, J. W., Department of Agriculture, Harrisburg, Pa.
Kerr, R. H., Bureau of Animal Industry, Washington, D. C.
Kimberly, C. H., 1319 H Street, N. W., Washington, D. C.
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REPORT ON PHOSPHORIC ACID.

By A. J. Patten (Agricultural Experiment Station, East Lansing, Mich.), *Referee*, and L. S. Walker (Agricultural Experiment Station, Amherst, Mass.), *Associate Referee.*

After carefully reviewing the work on basic slag for the past two years, it seemed unwise to continue along the same lines until at least a general survey and summing up of the situation could be made.

In 1911 two methods for total phosphoric acid were tried, the official gravimetric method using (a_7) method of making solution and a special method which called for the direct precipitation of the phosphoric acid with magnesia mixture in the presence of citrate of ammonia. Three methods for determining the available phosphoric acid were also tested, namely, the molybdate method, which is essentially the same as the official gravimetric method, the citrate of ammonia-magnesia mixture method, and the iron citrate of ammonia-magnesia mixture method. The results obtained by the various collaborators showed no consistent agreement by these methods. For example, seven analysts by the official gravimetric method on Sample 1 obtained results varying from 17.54 to 17.98 per cent, a difference of 0.44 per cent; two analysts obtained results, 18.22 and 18.60 per cent, a difference of 0.38 per cent, while two analysts working in the same laboratory obtained results varying from 18.88 to 19.25 per cent, a difference of 0.37 per cent. The maximum difference of all the analysts was 1.34 per cent. This same condition prevailed with all the other methods on both samples.

In 1912, two methods for total phosphoric acid were used, the official gravimetric method using the (a_4) method of making solution and the official gravimetric method using the (a_7) method of making solution. For available phosphoric acid the methods tested were the molybdate method, the optional volumetric method, and the citrate of ammonia-magnesia mixture method. In the determination of total phosphoric acid on three slags, the results in all cases did not show close agreement. The method using (a_7) solution gave the lowest results, the other method gave on the average higher results in cases when sulphuric acid was used as a solvent than when hydrochloric acid and nitric acid were used. In the determination of available phosphoric acid the results on Samples 1 and 2 do not agree as closely as might be desired, while those on Sample 3 agree very closely.

In 1913 three modifications of preparing the solution for the official gravimetric method were tested, namely, (a_4), (a_7), and (a_7) plus dehydration. In addition, the optional volumetric method was tried. For available phosphoric acid, the methods used the previous year were again tested.

The results obtained by the collaborating chemists showed no better agreement than the previous year. On Sample 3, by the (a_7) official gravimetric method, nine chemists obtained results varying from 13.96 to 14.47 per cent, a difference of 0.51 per cent; ten chemists obtained results varying from 14.57 to 14.88 per cent, a difference of 0.31 per cent; one chemist obtained 13.05 per cent and another chemist obtained 15.11 per cent, the maximum variation being 2.06 per cent. This example is typical of the results obtained by the other methods.

It is the opinion of the referee that the variations in the determination of total phosphoric acid have been due to the fact that the amount of iron being carried down with the yellow precipitate is not constant. It is possible that manganese may act in much the same way as the iron although this point has not been well established. In order to eliminate the contaminating influence of the iron in the gravimetric method, it was suggested that the addition of a small amount of sodium acetate to the solution before precipitating with magnesia mixture might hold the iron in solution. Preliminary work by the referee along this line gave very satisfactory results and this modification of the official method, was, therefore, included in the instructions sent to the collaborators this year. The influence of the iron in the volumetric method may be eliminated by standardizing the solutions against a standard phosphate material of approximately the same composition as the sample to be worked on. Attention was not called to this point in the instructions sent out this year but it so happened that all the collaborators followed practically this procedure. In all future work, attention should be given to this matter.

The citric acid solution of basic slag contains from 95 to 100 per cent of all the silica, 80 to 90 per cent of the calcium and 10 to 20 per cent of the iron. Therefore, the same variations may be expected in the results for available phosphoric acid by the molybdate and volumetric methods as were obtained for total phosphoric acid and, furthermore, the effect of the iron may be eliminated by the modifications mentioned.

According to M. Popp,[1] the soluble silica does not affect the results except when the amount of soluble iron is small. On the basis of his investigations on this subject Popp proposed the iron citrate method, which is similar to the iron citrate of ammonia-magnesia mixture method tried by this association two years ago except that ferric chlorid is used

[1] Chem. Ztg., 1912, **36**: 1102.

instead of ferrous chlorid and, in addition, 10 cc. of 0.3 per cent hydrogen peroxid solution are added to oxidize any sulphid that may be present. Attention has been given to another method known as the Lorenz method, that has been tried out very extensively by the German experiment stations. In this method the yellow precipitate, after filtering, is dried in a partial vacuum and weighed. The results obtained in the preliminary work by both the iron citrate and Lorenz methods gave excellent results and were, therefore, included in the work for this year.

At the request of the chairman of the Committee on Availability of Phosphoric Acid in Basic Slag, the work has been conducted on the same slags as used by that committee. Four samples of slag marked A, B, C, and D were thoroughly mixed and sent to eight chemists who had previously signified their willingness to coöperate in the work. The samples were numbered as follows: Sample 1 corresponding to Slag C, Sample 2 corresponding to Slag A, Sample 3 corresponding to Slag D, Sample 4 corresponding to Slag B.

In addition to the four slags a synthetic solution, Sample 5, representing as closely as possible the citric acid solution of an average basic slag, was sent out. This solution contained in each 100 cc.: 1.5 grams of ammonium phosphate, 5 grams of calcium chlorid, 10 grams of citric acid, 1.12 grams of ferric chlorid, and 8.8 cc. of sodium silicate (10 per cent).

On account of the preliminary work done on these methods by the referee it was impossible to send the samples out as early as was hoped and this fact is probably responsible for so few chemists participating in the work.

The following instructions were sent to each collaborator:

INSTRUCTIONS FOR COLLABORATORS.

Samples 1, 2, 3, and 4 are basic slags used by the special committee.

Sample 5 is a synthetic solution containing a known amount of phosphoric acid. The methods outlined under available phosphoric acid only, are to be used for Sample 5.

A. Determine moisture in Samples 1, 2, 3, and 4 at 100° C.

B. Determine total phosphoric acid in Samples 1, 2, 3, and 4 by each of the following methods:

(a) *Official gravimetric method*, using (a_7) method of making solution (Bur. Chem. Bul. 107, Rev., p. 2). Dehydrate an aliquot (20 cc.) of the basic slag solutions by evaporating to dryness on a steam or hot water bath; take up with 5 cc. of hydrochloric acid and 25 cc. of hot water; digest to complete solution and filter off silica (SiO_2). From this point proceed as directed for determination of total phosphoric acid (Bur. Chem. Bul. 107, Rev., p. 3). Before precipitating with magnesia mixture, add 5 cc. of 5 per cent sodium acetate.

(b) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of solutions (a_7) by the optional volumetric method (b) (Bur. Chem. Bul. 107, Rev., p. 4).

(c) *Lorenz method* (Landw. Versuchs-Stat., 1901, **55**: 183).—Dissolve 2 grams of basic slag in 15 cc. of concentrated sulphuric acid and 5 cc. of concentrated nitric

acid, cool and make up to 200 cc. Into a 200 to 250 cc. beaker measure carefully 20 cc. of the solution and add enough nitric acid (specific gravity 1.20) to bring the volume to 50 cc. Heat the solution, without stirring, over a wire gauze until the first air bubbles appear. Take from the flame and rotate a few times so that the sides of the beaker will not be overheated and add at once, into the middle of the solution, 50 cc. of the sulpho-molybdate reagent. After the precipitate has settled to the bottom, 5 minutes at the longest, stir vigorously for one-half minute with a glass rod. Cover the beaker and allow to stand overnight. Filter through a platinum or porcelain Gooch crucible using a single thickness of ash- and fat-free filter paper in the bottom. If the paper is cut so that it just fits the bottom of the crucible without turning up on the sides, no trouble will be experienced with the precipitate running through. Wash the precipitate four or five times with 2 per cent ammonium nitrate solution and carefully transfer all the yellow precipitate to the crucible. Then wash the precipitate by filling the crucible once full and twice half full with 95 per cent alcohol and allowing it to run dry after each addition. Next wash with ether in the same manner. Place the crucibles containing the precipitates in a fairly large desiccator (without sulphuric acid or calcium chlorid), exhaust to 100 to 200 mm. pressure, and allow to remain one-half hour before weighing. The weight of ammonium-phosphomolybdate multiplied by the factor 0.03295 gives the amount of phosphoric acid (P_2O_5).

NOTE.—The solution of basic slag prepared by the (a_7) method may be used but in this case the aliquot portion must be made up to 50 cc. with the sulphuric-nitric acid mixture described for this method under available phosphoric acid.

Preparation of reagents. Sulpho-molybdate solution.—In a 2 liter glass cylinder add 100 grams of pure, dry ammonium sulphate and 1,000 cc. of nitric acid (specific gravity 1.36) and stir until the sulphate is dissolved. In a 1,000 cc. flask dissolve 300 grams of pure dry ammonium molybdate in hot water, cool to about 20° C., fill to the mark, and pour in a thin stream into the nitric acid-ammonium sulphate solution. Allow to stand 48 hours at room temperature, filter through acid-resistant paper and preserve in a glass-stoppered bottle in a cool, dark place.

C. Determine available phosphoric acid as follows:

Concentrated solution of citric acid (10 per cent).—Dissolve in water exactly 200 grams of chemically pure crystallized citric acid having its full percentage of water of crystallization. Make up to exactly 2 liters. (If a large number of analyses are to be made, 0.5 gram of salicylic acid should be added to the liter of this solution to prevent decomposition.)

Dilute solution of citric acid (2 per cent).—Mix exactly 1 volume of the concentrated citric acid solution with 4 volumes of water. The resulting solution should have a temperature of about 17.5° C. when used.

Making citric solution.—Weigh 5 grams of the basic slag, transfer to a one-half liter Wagner flask containing 5 cc. of 95 per cent alcohol. The flask should have a neck width of at least 20 mm. and be marked at least 8 cm. below the mouth. Make up to the mark with dilute citric acid solution (2 per cent) of a temperature of 17.5° C. Fit the flask with a rubber stopper and put at once into the rotary apparatus for 30 minutes, making 30 to 40 revolutions per minute. Take off and filter immediately.

Analyses of the citric solution.—As soon as the filtration is completed, analyze according to the following methods. Dilute 100 cc. of Sample 5 to 500 cc. and, in every case, use same amount of this solution as is used of basic slag solution.

(a) *Molybdate method* (provisionally adopted 1911).—To 50 cc. of the clear filtrate add 100 cc. of molybdate solution made according to the official methods. Put the

beaker into a water bath until the temperature reaches 65° C., take out and allow to cool at ordinary temperature. Then filter, and wash the yellow precipitate of phosphomolybdate of ammonia four or five times with 1 per cent nitric acid. Dissolve in 100 cc. of 2 per cent ammonium hydroxid (cold), nearly neutralize with hydrochloric acid, and add to the solution 15 cc. of magnesia mixture (made according to the official method) drop by drop during continuous stirring. After 15 minutes add 10 to 12 cc. of ammonium hydroxid solution (specific gravity 0.90), then cover the beaker with a glass cover and allow to stand about 2 hours. Filter the double phosphate of ammonia and magnesia through a tared platinum Gooch crucible, wash six times with 2 per cent ammonium hydroxid, dry and proceed as customary for phosphoric acid determinations.

NOTE: Better results will be obtained if a smaller aliquot is taken and it is suggested that 20 to 25 cc. be used. Before precipitating with magnesia mixture add 5 cc. of 5 per cent sodium acetate solution.

(b) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of the clear solutions by the optional volumetric method (Bur. Chem. Bul. 107, Rev., p. 4, (b)).

(c) *Lorenz method.*—This method is conducted in exactly the same manner as for total phosphoric acid with one exception. The solution of basic slag (20 cc.) is made up to 50 cc. with the sulphuric-nitric acid mixture, prepared by mixing 30 cc. of sulphuric acid (specific gravity 1.84) with 1 liter of nitric acid (specific gravity 1.20).

(d) *Iron citrate method* (Landw. Versuchs-Stat., 1913, **79–80:** 260).—To 50 cc. of the citric acid solution of basic slag add in succession 25 cc. of the iron-citrate solution, 10 cc. of 0.3 per cent hydrogen peroxid, and 25 cc. of magnesia mixture. Put under stirring apparatus from 15 to 30 minutes, filter, ignite and weigh. It is suggested that the solutions be put under the stirring apparatus before the magnesia mixture is added and that the magnesia mixture be added rather slowly.

Iron citrate solution.—Place 1,000 grams of citric acid in a porcelain evaporating dish and pour over it a solution of iron chlorid containing 30 grams in 50 cc. of water. Slowly, and carefully add 4,000 cc. of 20 per cent ammonium hydroxid. After all has dissolved pour into 5,000 cc. flask and when cold fill to mark with water. Filter before using.

Magnesia mixture.—Dissolve 550 grams of magnesium chlorid and 700 grams of ammonium chlorid in a 10 liter flask with about 2,000 cc. of water. After the solution is complete add 1,750 cc. of 20 per cent ammonium hydroxid and fill to mark with water. Filter after several days standing.

PRECAUTIONS AND FURTHER INFORMATION.

(1) A photograph and detailed drawings of an inexpensive but efficient shaking apparatus were sent out by the referee for 1911. A copy will be forwarded to anyone coöperating in this work this year, on request to L. S. Walker, Amherst, Mass.

(2) The rotary apparatus prescribed for shaking the flasks must not be replaced by ordinary shaking or rocker apparatus as the latter differs in construction and effect. The rotary apparatus must turn around its axle 30 to 40 times per minute. Variations within these limits has no marked influence on the results.

(3) The half-liter flasks (after the design of Wagner) must have a neck width of at least 20 mm. and are marked at least 8 cm. below the mouth. These two points are important since if the neck width is too narrow and the mark too high the result

will be too low, owing to the movement of the liquid being so limited. (The proper flasks are listed in E. & A. Catalogue, (1913) 3172.)

(4) The filtration must be done immediately after 30 minutes' rotation, and it is best to use the folded filter paper of such size that the whole quantity of the liquid can be poured onto the filter at once. Small and bad filtering papers give rise to error in consequence of too slow filtration. If at first the filtrate is not clear, it must be filtered again (through the same filter) until it becomes clear.

(5) If the beaker containing the mixture of phosphatic and molybdic solutions is put into the water bath until the temperature reaches between 60° and 70° C., a precipitate free from silicic acid results. If heating is continued for a much longer time the precipitate will often be mixed with silicic acid, especially when the molybdic solution is not added to the filtrate immediately but only after 6 to 12 hours (or longer) after filtration. If silicic acid is present, the precipitate dissolves slowly in ammonium hydroxid, but at first not clearly. Special attention must be paid to the point that the yellow precipitate is dissolved quickly and quite clearly by ammonium hydroxid (2 per cent) not made warm. If the solution becomes clear only after some time, molybdic solution and nitric acid must be added to same in order to get a pure precipitate of phosphomolybdate of ammonia, that is, the phosphoric acid must be reprecipitated by the molybdic solution.

RESULTS OF COLLABORATION.

Comparative work on basic slag.

SAMPLE AND ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID: Official gravimetric method	TOTAL PHOSPHORIC ACID: Optional volumetric method	TOTAL PHOSPHORIC ACID: Lorenz method	AVAILABLE PHOSPHORIC ACID: Molybdate method	AVAILABLE PHOSPHORIC ACID: Optional volumetric method	AVAILABLE PHOSPHORIC ACID: Lorenz method	AVAILABLE PHOSPHORIC ACID: Iron citrate method
SAMPLE 1:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. S. Lykes, Clemson College, S.C.	0.16	13.27	13.30	13.22	12.77	12.25	12.65	12.77
	......	......	......	....	12.73	12.34	12.50	12.70
	......	......	......	....	12.37	12.39	12.43	......
	......	......	......	....	12 45	12 36	12.65	......
Average	0.16	13.27	13.30	13.22	12.58	12.34	12.56	12.74
O. B. Winter, East Lansing, Mich.	0.28	......	13.05	13.10	......	12.75	12.80	12.66
	......	......	13.00	13.00	......	12.65	......	12.72
Average	0 28	......	13.03	13.05	......	12.70	......	12.69
O. F. Jensen, East Lansing, Mich.	0.21	13.04	12.85	12.73	12 62	12.70	12.55	12.68
	......	13.07	12.95	12.75	12.76	12.65	12.55	12.74
Average	0.21	13.06	12.90	12.74	12.69	12.68	12.55	12.71
Paul Rudnick and W. L. Latshaw, Chicago, Ill.	0.13	13.44	13.29	13.08	12.72	12.57	12.58	12.83
	0.15	13.32	13.32	13.09	12.79	12.60	12.55	12.80
	......	13.04	13.34	13.15	12.81	12.83	12.80	12.72
	......	13.19	13.30	13.17	12.87	12.77	12.81	12.70
Average	0.14	13.25	13.32	13.13	12.80	12.70	12.69	12.77
	......	......	......	[1]13.01	......	......	......	......
	......	......	......	[1]12 91	......	......	......	......
Average	......	......	......	[1]12 98	......	......	......	......

[1] Sulphuric acid digestion.

Comparative work on basic slag—(Continued).

SAMPLE AND ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID			AVAILABLE PHOSPHORIC ACID			
		Official gravimetric method	Optional volumetric method	Lorenz method	Molybdate method	Optional volumetric method	Lorenz method	Iron citrate method
SAMPLE 2:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. S. Lykes	0.26	18.20	18.17	18.24	15.33	15.11	15.25	15.40
	.....	.....	.....	.....	15.40	15.05	15.29	15.42
	.....	.....	.....	.....	15.15	14.91	.....	.....
	.....	.....	.....	.....	15.09	14.94	15.23	.....
Average	0.26	18.20	18.17	18.24	15.24	15.00	15.26	15.41
O. B. Winter	0.23	.....	18.00	18.05	.....	15.50	15.40	15.29
	.....	.....	17.95	17.95	.....	15.50	15.45	15.24
Average	0.23	.....	17.98	18.00	.....	15.50	15.43	15.27
O. F. Jensen	0.30	18.46	18.10	18.08	15.42	15.17	15.15	15.30
	.....	18.36	18.05	17.90	15.26	15.21	15.10	15.31
Average	.....	18.41	18.08	17.99	15.34	15.19	15.13	15.31
Paul Rudnick and W. L.	0.19	18.44	18.17	17.98	15.46	15.25	15.28	15.21
Latshaw	0.18	18.50	18.17	17.96	15.53	15.25	15.32	15.14
	.....	18.14	18.22	18.20	15.49	15.35	15.52	15.24
	.....	18.34	18.17	18.14	15.51	15.35	15.47	15.27
	0.19	18.36	18.19	18.07	15.50	15.30	15.40	15.22
	.....	.....	.....	[1]17.87	.....	.....	.....	.....
	.....	.....	.....	17.83	.....	.....	.....	.....
Average	.....	.....	.....	[1]17.85	.....	.....	.....	.....
SAMPLE 3:								
C. S. Lykes	0.19	15.59	15.24	15.09	13.78	13.40	13.55	13.73
	.....	.....	.....	.....	13.66	13.42	13.60	13.67
	.....	.....	.....	.....	13.70	13.50	13.87	.....
	.....	.....	.....	.....	13.70	13.50	13.87	.....
Average	0.19	15.59	15.24	15.09	13.71	13.46	13.72	13.70
O. B. Winter	0.23	.....	14.92	14.90	.....	13.73	13.65	13.96
	.....	.....	14.97	14.75	.....	13.78	13.70	13.84
Average	0.23	.....	14.95	14.83	.....	13.76	13.67	13.90
O. F. Jensen	0.26	15.72	14.83	.....	13.75	13.73	13.70	13.90
	.....	15.34	14.97	14.80	13.77	13.78	13.65	13.82
Average	0.26	15.53	14.90	14.80	13.76	13.76	13.68	13.68
Paul Rudnick and W. L.	0.20	15.23	14.95	14.88	13.70	13.70	13.71	13.66
Latshaw	0.19	15.20	15.06	14.95	13.83	13.68	13.73	13.64
	.....	15.41	15.19	15.19	13.82	13.71	13.78	13.76
	.....	15.30	15.25	15.21	13.76	13.76	13.78	13.71
Average	0.20	15.29	15.11	15.06	13.78	13.72	13.75	13.69
	.....	.....	.....	[1]14.96	.....	.....	.....	.....
	.....	.....	.....	[1]14.98	.....	.....	.....	.....
Average	.....	.....	.....	[1]14.97	.....	.....	.....	.....

[1] Sulphuric acid digestion.

Comparative work on basic slag.—(Concluded).

SAMPLE AND ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID: Official gravimetric method	TOTAL PHOSPHORIC ACID: Optional volumetric method	TOTAL PHOSPHORIC ACID: Lorenz method	AVAILABLE PHOSPHORIC ACID: Molybdate method	AVAILABLE PHOSPHORIC ACID: Optional volumetric method	AVAILABLE PHOSPHORIC ACID: Lorenz method	AVAILABLE PHOSPHORIC ACID: Iron citrate method
SAMPLE 4:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. S. Lykes	0.21	18.82	18.65	18.57	14.66	14.18	14.42	14.69
	......	......	......	......	14.32	14.01	14.39	14.43
	......	......	......	......	14.29	14.10	14.45	......
	......	......	......	......	14.17	14.18	14.51	......
Average	0.21	18.82	18.65	18.57	14.36	14.12	14.44	14.56
O. B. Winter	0.23	......	18.45	18.30	......	14.43	14.55	14.50
	......	......	18.40	18.35	......	14.37	......	14.54
Average	0.23	......	18.43	18.33	......	14.40	......	14.52
O. F. Jensen	0.24	18.94	18.40	18.35	14.39	14.24	14.25	14.31
	......	18.87	18.30	18.25	14.35	14.34	14.30	14.35
Average	0.24	18.91	18.35	18.30	14.37	14.29	14.28	14.33
Paul Rudnick and W. L.	0.23	18.83	18.42	18.33	14.79	14.57	14.53	14.50
Latshaw	0.22	18.85	18.42	18.30	14.69	14.51	14.50	14.39
	......	18.67	18.53	18.42	14.75	14.58	14.62	14.44
	......	18.65	18.48	18.40	14.68	14.63	14.57	14.48
Average	0.23	18.75	18.47	18.37	14.73	14.57	14.56	14.45
	......	......	......	[1]18.26	......	......	......	......
	......	......	......	[1]18.22	......	......	......	......
Average	......	......	......	[1]18.24	......	......	......	......

ANALYST	AVAILABLE PHOSPHORIC ACID: Molybdate	Optional volumetric	Lorenz	Iron citrate
SAMPLE 5:	*grams per 100 cc.*	*grams per 100 cc.*	*grams per 100 cc.*	*grams per 100 cc.*
C. S. Lykes	....	0.165	0.16689	0.16532
	....	0.165	0.16676	0.16508
Average	....	0.165	0.16683	0.16520
O. B. Winter	....	0.1708	0.1700	0.1680
	....	0.1688	....	....
Average	....	0.1694	0.1700	0.1680
O. F. Jensen	0.16730	0.1668	0.1650	0.16552
	....	0.1678	....	....
Average	0.16730	0.1673	0.1650	0.16552
Paul Rudnick and W. L. Lat-	0.1659	0.1638	0.1643	0.1651
shaw[1]	0.1642	0.1643	0.1640	....
Average	0.16505	0.16405	0.1642	0.1651

[1] Sulphuric acid digestion.
[2] Theory, 0.16584 gram of phosphoric acid in 100 cc. of sample.

COMMENTS OF ANALYSTS.

C. S. Lykes: The instructions were followed exactly except in the case of heating the solutions of ammonium phosphomolybdate, which were raised to a temperature of 50° to 60° C. at the start and then stirred for 20 minutes at approximately 850 revolutions per minute. In preparing the solution of citric acid, it was found that our citric acid did not contain the full amount of water of crystallization. A solution of citric acid was therefore made up and standardized to exactly 2 per cent, on the basis of the full amount of water of crystallization, by means of a standard solution of caustic soda of 0.14679 normal strength. In the volumetric determinations a standard solution of caustic soda was used. This solution had been standardized by samples of phosphate rock which were put into solution by (a_4), official method, Bulletin 107, Revised, using 20 cc. of sulphuric acid.

Paul Rudnick: It was interesting to note that the citric acid solutions of Samples 2 and 3 showed a precipitation similar to that in the synthetic solution, Sample 5, while Samples 1 and 4 did not. It was also noted that there was some difficulty in digesting these samples of basic slag for the determination of total phosphoric acid, the slag showing a tendency to form a lump which was not easily wet by the acid. The addition of a little water to the dry sample in the flask, so that the entire powder was thoroughly moistened before adding the acid, obviated the difficulty entirely.

DISCUSSION OF RESULTS.

The results obtained this year are very satisfactory and encouraging, the greatest variation being 0.62 per cent on Sample 4.

Official gravimetric and molybdate methods.—The proposed modification for these methods was not carried out as intended owing to an error in the instructions but the results obtained in the referee's laboratory by adding 5 cc. of 5 per cent sodium acetate solution before precipitating with magnesia mixture were very good. This modification should be given another trial.

Optional volumetric method.—The results by this method show a better agreement than those obtained in either 1912 or 1913. This may be attributed to the fact that all the collaborators used a standard alkali solution that had been standardized against a standard phosphate rock. Attention should be given to this point in the future work.

Lorenz method.—This method possesses some advantages over the official gravimetric and molybdate methods and the results obtained by it agree quite as well as by the other methods. It is rapid and comparatively simple; the chief objection is the cost of the reagents.

In this connection it is interesting to note that the method devised some years ago by T. S. Gladding and reported by A. G. Stillwell in The Chemist-Analyst, 1914, number 10, page 20, is similar to the Lorenz method but simpler of manipulation and less expensive. It is suggested that the referee for next year make a comparison of the two methods.

Iron citrate method.—The most consistently-agreeing results were obtained by this method, the greatest variation being 0.38 per cent on Sam-

ple 4. The method is rapid, easily worked and the precipitates are clean and comparatively free from impurities.

On Sample 5 the results by all the methods are exceedingly close, the greatest variations being obtained by the volumetric and Lorenz methods.

BIBLIOGRAPHY.

The following incomplete bibliography of the more recent work on basic slag is made a part of the report.

Chem. Ztg., 1912, **36**: 937; 1037; 1102.
Ibid., 1913, **37**: 145.
Landw. Versuchs.-Stat., 1901, **55**: 183.
Ibid., 1913, **79-80**: 229.
Ibid., 1913, **81**: 160.
Ibid., 1913, **82**: 465.
Landw. Jahrb., 1913, **45**: 119; 327.
Zts. anal. Chem., 1912, **51**: 161.
Zts. angew. Chem., 1902, **15**: 1133.
Bied. Zent. Agr. Chem., 1913, **42**: 363.

RECOMMENDATIONS.

It is recommended—

(1) That further work be done on the methods for basic slag as reported this year.

(2) That special attention be given to standardizing the alkali solution used in the volumetric method.

(3) That the methods be tried on as many different samples as possible.

REPORT ON NEUTRAL AMMONIUM CITRATE.

By L. S. Walker (Agricultural Experiment Station, Amherst, Mass.), *Associate Referee*.

Committee A recommended, at the last meeting of the association, in 1913, that the referee on phosphoric acid make a study of the preparation of neutral ammonium citrate by the titration method. In accordance with this recommendation the referee, A. J. Patten, requested the associate referee to take charge of this work. In the studies undertaken two methods of preparing the neutral ammonium citrate solution were employed. On April 1, 1914, three prepared fertilizer samples, together with the following outline or plan, were sent to seven chemists who had previously signified their intention of coöperating in the work.

INSTRUCTIONS TO COLLABORATORS.

PREPARATION OF NEUTRAL AMMONIUM CITRATE.

A. Determine moisture at 100° C.

B. Determine the insoluble phosphoric acid by the official method as described in Bureau of Chemistry Bulletin 107, Revised, page 3, under (4) (*a*) using (*b*) method for making solution.

The neutral ammonium citrate solutions to be used in the above method are prepared as follows:

Solution I. Titration method.—Dissolve 370 grams of commercial citric acid in 1,500 cc. of water; add 358.33 cc. of ammonium hydroxid (specific gravity 0.90) and allow to cool. Carefully measure 50 cc. of this citrate solution into a 250 cc. flask, make up to the mark with distilled water and shake thoroughly. Then measure (preferably by means of a burette) 5 cc. of the diluted solution into a beaker, add 4 cc. of a perfectly neutral 40 per cent solution of formaldehyde and titrate with tenth-normal sodium hydroxid using phenolphthalein as an indicator. The pink color should remain after the solution is brought to boiling. Determine the ammonia in 5 cc. of the diluted solution in the usual manner by distilling with magnesia. The difference between the acid and ammonia titration gives the number of cubic centimeters of tenth-normal ammonia required to neutralize 1 cc. of the acid citrate solution, from which the amount of a stronger solution of ammonium hydroxid required to neutralize any given amount of the acid solution may be easily calculated.[1]

To illustrate this method, it was found that 5 cc. of the diluted solution equivalent to 1 cc. of the citrate solution required 28.65 cc. of tenth-normal sodium hydroxid and 27.62 cc. of tenth-normal sulphuric acid. Therefore the difference between the acid titration, 28.65 cc., and the ammonia titration, 27.62 cc. is 1.03 cc. Consequently 1 cc. of the citrate solution requires 1.03 cc. of tenth-normal ammonia to make it exactly neutral. Take a 5 per cent solution of ammonium hydroxid and find its titration in terms of tenth-normal sulphuric acid. Then with this data can be figured the number of cubic centimeters of 5 per cent ammonium hydroxid required per liter of citrate solution to neutralize exactly. Dilute the perfectly neutralized solution so that the specific gravity will be 1.090 at 20° C., testing by means of a Westphal balance or by a pycnometer.

According to Patten's article in the Journal of Industrial and Engineering Chemistry, a strictly neutral solution of ammonium citrate of exactly 1.090 specific gravity should give the following results: 1 cc. of citrate solution gives 26.34 cc. of tenth-normal ammonia; 1 cc. of citrate solution gives 26.33 cc. of tenth-normal citric acid, equivalent to 44.76 grams of ammonia per liter, equivalent to 168.57 grams of citric acid per liter. Ratio of ammonia to citric acid is 1 to 3.766.

Solution II. Litmus method.—Dissolve a convenient quantity of commercial citric acid in four times its weight of water; add commercial ammonium hydroxid until a faint odor of ammonia persists when the solution is hot; cool and complete the neutralization as follows: Select four Nessler's jars in which equal volumes occupy equal heights, add a carefully purified litmus solution from a burette, taking care that precisely the same volume of indicator is placed in each of the four jars (about 2 cc.). Fill two of the jars to the 50 cc. mark with distilled water neutral to the indicator; add to each of the remaining jars from a burette 2.5 to 5 cc. of the citrate solution to be neutralized, and fill to the 50 cc. mark. Mix well, place the jars containing the indicator and water alone one in front of the other; add to one a drop of strong citric acid solution and to the other a drop of strong ammonium hydroxid. By looking through both of these jars the neutral tint of the indicator is observed for comparison. Arrange the jars containing the ammonium citrate to be tested in a similar manner and compare the colors; add citric acid or ammonium hydroxid until the tint produced can not be distinguished from that observed through the pair of jars used for a standard neutral color. It is recommended that the pairs of jars be placed in a box divided into compartments. Narrow slits through each compartment will aid in the comparison of the tints. Bring the neutralized

[1] Method practically as given in J. Ind. Eng. Chem., 1913, **5**: 567.

citrate solution to a specific gravity of 1.090 at 20° C., testing by means of a Westphal balance or by a pycnometer.[1]

When both the above solutions of ammonium citrate are neutralized and prepared, carefully analyze them by the titration method to determine the ratio of ammonia to anhydrous citric acid and report results to the associate referee, together with the analyses of the three fertilizer samples, not later than September 1, 1914.

RESULTS OF COLLABORATION.[2]

Analyses of three fertilizers.

Analyst	Moisture at 100° C.			Insoluble phosphoric acid						Ratio of ammonia to citric acid	
				Titration method			Litmus method			Titration method	Litmus method
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3		
E. G. Proulx, Lafayette, Ind.	5.59	6.25	8.85	11.29	0.28	2.47	10.81	0.26	2.08	[1]1:3.753	[1]1:3.821
R. B. Deemer, Lafayette, Ind.	5.45	6 09	9.03	11.23	0.33	2.34	10 83	0.29	1.99	[1]1:3.753	[1]1:3.821
C. P. Jones and L. S. Walker, Amherst, Mass.	5.60	8.01	9.50	10.15	0.40	2.00	6.80	0.26	1.39	1:3.812	1:3.907
				Azolitmin method			Tenth-normal citric acid				
Paul Rudnick and W. L. Latshaw, Chicago, Ill.				10.65	0.40	2.12	11.00	0.58	2.09	.	.
				10.16	0.38	1.84	11.10	0.52	1.84		
				10.32	0.40	2.02	11.02	0.58	2.02		
	5.45	8.58	8.85	10.38	0.39	1.99	11.04	0.56	1 98		

[1] Average of two analysts.

COMMENTS OF ANALYSTS.

E. G. Proulx and R. B. Deemer:—On addition of the calculated amount of ammonia as shown by titration, to make a neutral citrate solution and repeating the titration we were unable to secure the theoretical amount of ammonia and found it necessary to make four separate additions before the titration gave the desired result. A moistened red litmus paper placed in the neck of a bottle of this solution, at room temperature, not in contact with the solution, gave a distinct alkaline reaction indicating loss of ammonia. The method provides no specific temperature for the solution when the aliquot is removed for titration. This it seems to us introduces a possible source of error and we would suggest that 20° C., the temperature at which the gravity is determined, be adopted. An additional source of possible error is also noted in the titration of citric acid in the presence of formaldehyde owing to the necessity for repeated neutralization with sodium hydroxid and the impossibility of duplicating titration closer than 0.1 cc. of tenth-normal sodium hydroxid equivalent to 0.64 gram of citric acid per liter.

With the litmus method we were successful with the first addition of the calculated amount of citric acid solution in preparing a solution neutral to purified

[1]Method practically as given in Bur. Chem. Cir. 52, p. 1.

[2]Complete results have been received from only two chemists.

litmus, though the analysis by the titration method showed less citric acid and ammonia than a neutral solution of ammonium citrate of exactly 1.09 specific gravity should contain as calculated by the referee.

Using the latest atomic weights we were unable to obtain the ratio of ammonia to citric acid of 1 to 3.766 but secured 1 to 3.758. If the burette reading (26.34 cc. of tenth-normal ammonia given in your instructions is calculated with the correct factor (0.0017034) for tenth-normal ammonia you will obtain an equivalent of 44.867 grams of ammonia per liter. Using this to calculate the ratio, 1 to 3.757 is obtained.

W. J. Jones, Jr.: In looking hurriedly over the instructions and results it seems to me that there are a number of places in the proposed method where appreciable errors are likely to occur. In the first place, I note that the method deals with chemically pure citric acid and ammonia and the results thus secured are applied to a commercial product which we have found quite variable and on which, it seems to me, the results may be very misleading. In the second place the actual amount of original solution taken for titration really amounts to 1 cc. so that in calculating the results to liters the working error is multiplied by 1,000. The instructions call for no additional titration after the calculated amount of ammonia is added. Proulx and Deemer, however, find that they are unable to secure the theoretical amount of ammonia under the conditions mentioned. I also believe that the pycnometer is much more accurate in taking the specific gravity of this solution than the Westphal balance, at least such has been our experience. It also occurs to me that the addition of a calculated amount of ammonia in any other way than by forcing it into the solution from the bottom will result in a loss of some ammonia since the latter is so volatile that it cannot be transferred by ordinary means without loss. The use of formaldehyde, of which we have been unable to obtain a solution that was neutral necessitating the addition of a neutralizing agent, also increased the chances for error.

Taken as a whole, therefore, it would seem that much more work was necessary to insure that the method will give the results expected of it. Undoubtedly the methods now in use by the association do not give concordant results. So far as the corallin method is concerned we have never had any one connected with this laboratory who could any more than guess at the neutrality of the citrate solution by this method. Practically since its adoption as the alternate method we have prepared our citrate by the alcoholic calcium chlorid method with exceptionally good results so far as uniformity of the ammonia content of the solution is concerned. The average specific gravity and ammonia content per liter of 112 ammonia citrate solutions prepared in this laboratory since March 8, 1899, give 1.09006 and 43.63 grams, the specific gravity of each being made with pycnometer. The ammonia in these solutions was determined by taking 25 cc. at 20° C., making up to a volume of 250 cc. at the same temperature and distilling the ammonia with magnesium oxid in the usual manner. These solutions have been prepared by a large number of analysts who have been able to secure concordant ammonia content by the method mentioned, the ratio of citric acid to ammonia in our solution being 1 to 3.846.

Using our regular solution on the samples submitted by you, Proulx and Deemer obtained the following results:

Sample	Per cent insoluble phosphoric acid (P_2O_5)
1	9.79
	9.74
2	0.29
	0.34
3	2.19
	2.13

The results in No. 1 you will note are appreciably lower than those with the titration citrate as well as the citrate prepared with litmus. While it is quite probable that the solution prepared with alcoholic calcium chlorid may be slightly acid on the basis of theoretical results our experience indicates that absolutely concordant results can be obtained with it from year to year and based on the report made by Proulx and Deemer regarding the formaldehyde method I believe more difficulty will be experienced with the latter than with the alcoholic calcium chlorid method.

C. P. Jones and L. S. Walker: There seems to be no difficulty in obtaining checks in the determination of ammonia by the magnesium oxid method, but we had some trouble in titrating the citric acid with tenth-normal sodium hydrate using formaldehyde. A blank was used and by titrating just to the turning point, then boiling, a uniform color resulted. In this way very good checks could be obtained.

Paul Rudnick and W. L. Latshaw: Only one solution of neutral ammonium citrate was prepared for this work, since we have been for some time preparing this solution for our regular work by a combination of the two methods described with slight modifications. In the titration method the modification consists merely in changing the quantities measured out. We make up 25 cc. of the ammonium citrate solution to 250 cc. and draw off aliquot portions of 25 cc. each for the determination of citric acid and ammonia. The indicator method is carried out in this laboratory as follows:

Prepare a small stock of 1 per cent azolitmin solution in water and keep it in a dropping bottle which has a small pledget of cotton in place of the usual rubber bulb in order to avoid mold. Add 3 cc. of this 1 per cent solution of azolitmin to 1,000 cc. of neutral, freshly-boiled and cooled distilled water, which will give a distinct, but not too deep color. Place five portions of 5 cc. each of the ammonium citrate solution to be tested in 50 cc. tall Nessler jars and make up to volume with the water containing azolitmin solution. To four of these tubes add 1.0 cc. and 0.5 cc. of tenth-normal ammonia and tenth-normal citric acid respectively and compare the colors of these with the fifth tube (to which nothing has been added) in the Craven-Jennings colorimeter.

We find that the triammonium citrate solution, which the analytical specifications contemplate, is practically neutral to azolitmin and that the two methods constitute excellent checks on each other. For this reason we are submitting but one set of results with neutral ammonium citrate solution. As a matter of interest, however, we are also submitting results obtained by the use of tenth-normal citric acid (J. Ind. Eng. Chem., 1914, **6**: 486).

It is evident that tenth-normal citric acid gives results which are quite comparable with those obtained by neutral ammonium citrate on Samples 2 and 3. In the case of Sample 1, in which the insoluble phosphoric acid content is comparatively high, the agreement is not quite so good, but there is just as much divergence in the individual results obtained by the neutral ammonium citrate as there is between those obtained by the two solutions.

These results are submitted with the request that the referee on phosphoric acid take up the determination of insoluble phosphoric acid from the standpoint of working out a suitable substitute for neutral ammonium citrate solution. As stated by us in the paper referred to, a dilute acid solution of suitable concentration is much more easily prepared, and it overcomes difficulties in filtration and washing inherent in the neutral ammonium citrate method. Moreover, it represents a considerable economy, particularly at the present time when citric acid can hardly be obtained at any price.

It was suggested by the referee that samples of neutral ammonium citrate from several laboratories be tested for their ammonia and citric acid ratio, and also to be used for the determination of the insoluble phosphoric acid on the three fertilizer samples prepared for the coöperative work. Four solutions were procured and results were obtained as follows:

SOLUTION	INSOLUBLE PHOSPHORIC ACID			RATIO OF AMMONIA TO CITRIC ACID
	Sample			
	1	2	3	
1	9.86	0.28	2.02	1 : 3.859
2	9.36	0.29	1.93	1 : 3.921
3	6.80	0.26	1.39	1 : 3.907
4	6.57	0.38	1.28	1 : 4.038

The difference between the highest and lowest test for insoluble phosphoric acid on Sample 1 (which was a complete fertilizer having a bone base) illustrates in a striking manner, the necessity of some uniform and accurate method of preparing the neutral solution of citrate of ammonia. A variation of 3.29 per cent of insoluble phosphoric acid as shown by the highest and lowest test on Sample 1 would mean a difference in valuation on this fertilizer of $2.53 per ton. Even Sample 3 which is a complete fertilizer with acid phosphate as a base, shows altogether too wide a variation in insoluble phosphoric acid by the various solutions in use in the several laboratories. Attention is called to the relatively wide variation existing in the ratio of ammonia to citric acid in the various solutions. It might be stated in this connection that citrate solution cannot be safely carried over from one season to another. A solution prepared in the Massachusetts experiment station laboratory in September, 1913, was analyzed in April, 1914, and its ratio was found to be 1 to 3.971, and when used in the analysis of fertilizer Sample 1, 8.85 per cent of insoluble phosphoric acid was obtained. These tests indicate that the solution had broken down, ammonia being lost, and showed a decided acid character.

CONCLUSIONS.

It seems unfortunate that a more hearty coöperation could not be secured from the association in this most valuable line of work. Reports were received from only four laboratories. These reports, however, show much care and thought by the various analysts and furnish many valuable suggestions which will hardly fail to be of great help to the referee in planning future work.

Although the variety of results obtained does not allow the drawing of any definite conclusions, yet they all emphasize the great importance of some more uniform and accurate method of preparing the neutral citrate of ammonia solution. The suggestion of Mr. Rudnick that some substitute for neutral citrate solution be studied, seems to possess more than ordinary merit.

RECOMMENDATIONS.

The associate referee would therefore recommend—

(1) That the titration method of preparing neutral citrate of ammonia solution receive further study.

(2) That the referee for 1915 be requested to plan work that will show the relative worth of substitute solutions in the determination of insoluble phosphoric acid in fertilizers.

TRIAMMONIUM CITRATE.

By Robert A. Hall (University of Minnesota, Minneapolis, Minn.).

The writer first prepared the salt, normal triammonium citrate, in 1911 shortly after the completion of the investigations which were expressed in the papers "The Physical Properties of Aqueous Solutions Containing Ammonia and Citric Acid" (J. Amer. Chem. Soc., 1911, **33:** 711) and the "Preparation of Neutral Ammonium Citrate Solutions by the Conductivity Method" (J. Ind. Eng. Chem., 1911, **3:** 559). The salt thus obtained reacted alkaline to rosolic acid (corallin), although the analyses showed it to have the composition of normal triammonium citrate. As this was contradictory to all the literature then existing on the subject it was deemed advisable to make further investigation. In the spring of 1912 further samples of the salt were made, analyzed, and certain physical and chemical properties were observed.[1] The method of preparation and general properties of the salt were reported, for the purpose of record, at the meeting of the Academy of Science of St. Louis, April 21, 1913.[2] An informal oral announcement of the preparation and properties of the salt was also made at the May meeting of the St. Louis section of the American Chemical Society. It was desired to continue the investigation of the salt along the following lines: (1) As to its physical chemical properties, it was deemed necessary to investigate experimentally the concentration of the ammonia and citric acid ions in both a dilute solution and in a solution of the concentration used in the fertilizer analysis; also, to ascertain by experimental research the proper indicator to be used in testing the neutrality of the "neutral" ammonium citrate solutions; (2) the character and effect of the growth that so frequently occurs in so-called neutral solutions of ammonium citrate; (3) the pharmacological properties of the salt.

[1] I am indebted to J. T. Ragsdale, Jr. and H. W. Ramsay, my students, of St. Louis, for their assistance in making these preliminary analyses.

[2] Trans. Acad. Sci. St. Louis, 1913, **22:** 40.

In the summer of 1913 the investigation of the physical chemical properties had been scarcely begun in the Kent Chemical Laboratory, University of Chicago, when Hildebrand's paper, "Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching"[1] appeared. Hildebrand had anticipated a part of the investigation desired and had announced his intention of investigating and determining the proper indicator for concentrated solutions of neutral ammonium citrate, so this part of the research was deferred. The recent appearance of his paper on "The Preparation of 'Neutral' Ammonium Citrate,"[2] enabled me to employ his results in the examination of the salt under investigation and to complete that part of it. Although the investigation of the growth formation in the solution and the pharmacological properties of the salt is still incomplete yet the importance of the salt, to the fertilizer chemist in particular, is thought to be sufficient justification for publishing the results so far obtained.

Hantsch found in his investigations of tautomeric salts that by passing perfectly dry ammonia gas into solutions of organic substances in perfectly anhydrous ether or benzol that tautomeric forms of chloramids, nitro derivatives, etc., hitherto regarded as unstable because of the dissociating effect of water, could be prepared and obtained pure in quantity. If proper care were taken to keep even traces of water from the compound until it had been freed from the mother liquor and perfectly dried, then these bodies were unaffected by moisture and could be freely exposed to the air. This suggested to me that triammonium citrate could be prepared by passing dry ammonia gas into a solution of citric acid altogether freed from the presence of water. This could be done by dissolving the anhydrous citric acid (made anhydrous by carefully heating the acid in vacuo to its melting temperature and carefully maintaining this temperature until the water of crystallization was completely removed) in an anhydrous solvent and then passing through the solution in excess a stream of perfectly dry ammonia gas. Since the diammonium citrate is soluble in boiling alcohol, absolute alcohol could be used as the solvent and precipitation would not occur until the formation of the triammonium citrate began. Moreover, only the pure triammonium salt would be obtained if the solution were kept at the boiling point until the acid had been completely converted into the normal salt. The yield would be quantitative. The normal salt could be freed from its mother liquor by decantation and by repeated washings with the anhydrous solvent, finally removing the last trace of the solvent by the suction of the filter pump. The salt, being thus perfectly dried, should be stable; it could then be exposed to the moisture of the air without undergoing decomposition.

[1] J. Amer. Chem. Soc., 1913, **35**: 847.
[2] J. Ind. Eng. Chem., 1914, **6**: 577.

Results obtained fully justified these conclusions. The solvent and washings could be freed from ammonia and recovered in the usual way, thus reducing the loss incurred in the preparation to that of the excess of ammonia gas used (and even this loss could be prevented by recovery of the ammonia).

EXPERIMENTAL.

Preparation of the normal triammonium citrate salt.—Citric acid was freed from its water of crystallization by heating it to 150° C., the melting point of the acid. The temperature was not allowed to go much above this point as the acid is decomposed by a higher heat. The removal of the water of crystallization was facilitated by the use of the vacuum pump. A weighed amount of this water-free acid was placed in a round-bottom flask whose mouth was sufficiently large to permit the use of a rubber stopper through which three tubes passed. One tube was for the admission of the ammonia gas; this tube extended nearly to the bottom of the flask and was slightly bent to avoid coming in contact with the extended flanges of the stirrer when in motion. Through the center of the stopper passed the stirrer which was propelled by a motor of a size sufficient to preclude the possibility of the stirrer stopping during the experiment. The third opening was for the entrance of the lower end of a reflux condenser tube which served the double purpose of an exit tube for the excess of ammonia gas and also for the condensation and return into the flask of the alcohol used as solvent, thus preventing the loss of alcohol. The upper end of the condenser was connected with a tightly-fitting tube which conducted the excess ammonia out of doors. The ammonia gas was obtained from a tank of liquid ammonia, or was prepared by allowing strong ammonia water to drop into a flask containing solid sodium hydroxid and ammonium chlorid. In either case, for the purpose of completely drying the ammonia, the gas was first passed through a reflux condenser and then through several upright towers filled with solid sodium hydroxid. Absolute alcohol, distilled over sodium, sufficient to dissolve completely the citric acid and also to cover completely the stirrer when in motion, was added and brought to the boiling temperature by heating on an electric bath. Ammonia gas was then slowly bubbled into the boiling solution which was being vigorously stirred by the electrically-propelled stirrer.

For some few minutes, dependent upon the concentration of the acid solution and upon the rate of admission of the gas, no precipitation occurred. This was as expected and was probably due to the formation of the mono- and diammonium citrates which are soluble in boiling alcohol. As soon as the formation of the triammonium citrate began, precipitation occurred and continued until all the acid had been converted

into triammonium citrate. When the precipitation was completed the heat was discontinued but the ammonia gas was allowed to pass through the solution until the flask had become entirely cool. This served to prevent air bearing water vapor from entering the flask as the flask cooled. The supernatant liquid was decanted from the salt and the salt washed several times by decantation with absolute alcohol until the washings were free from ammonia, finally being pressed dry on the Büchner funnel, using the rubber dam cover with the suction pump as suggested by Gortner.[1] The salt was further pressed out on a clay plate, dried for an hour on a dry steam bath, and then placed in a desiccator over sulphuric acid for 24 hours. The yield of triammonium citrate was quantitative. The alcohol used as solvent and washings was freed from ammonia and recovered in the usual way, thus making the only loss in the preparation that of the excess of ammonia used.

The method of preparation was varied by substituting for anhydrous citric acid Kahlbaum's purest citric acid, containing one molecule of water of crystallization. Otherwise the preparation was carried out as given. It was a great surprise to me that so pure and stable a salt was obtained. The yield, however, was not quantitative as much of the salt adhered to the sides of the flask. The yield was about 85 per cent.

Again the method of preparation was varied by omission of the use of the electrically-propelled stirrer. The flask was shaken by hand from time to time. There was observed a tendency of the precipitate to clog and stick to the walls of the flask. The flask was tightly corked and allowed to stand for a week. It was found that the salt obtained was the normal triammonium citrate. The yield was not over 75 per cent.

Another variation in the method of preparation was introduced by the substitution of ordinary 95 per cent alcohol for the absolute alcohol, the other conditions remaining as given in the first method of preparation. From 60 grams of anhydrous citric acid about 30 grams of the normal salt were obtained. As the mixture of the di and triammonium citrates adhered closely to the walls of the flask, it was easy to separate the pure salt. (While it has not been tried out yet it is very likely that the citric acid with its water of crystallization can be used in this method also.)

PROPERTIES OF TRIAMMONIUM CITRATE.

Triammonium citrate, prepared from a solution of the anhydrous citric acid in absolute alcohol or from a solution of pure citric acid containing water of crystallization in absolute alcohol, is a beautiful white, microscopically-crystalline salt. It is stable in so far that it can be exposed to the air for more than 24 hours without material change, can be

[1] J. Amer. Chem. Soc., 1914, **36**: 1967.

heated for an hour or more on a dry steam bath, or kept indefinitely in a desiccator over sulphuric acid. It is exceedingly soluble in water and can not be recrystallized from a water solution by evaporation. When a saturated water solution, cooled in a freezing mixture of ice and salt is poured into absolute alcohol similarly cooled, a mass of long, beautiful crystals is obtained; these are doubtless the triammonium citrate salt with one or more molecules of water of crystallization. They were very unstable and were not analyzed. McCandless in a recent publication states that he has prepared a triammonium citrate $(NH_4)_3C_6H_5O_7$, in a similar way. Because of the instability of his salt it is likely that it contained one or more molecules of water of crystallization. It is hoped to take advantage of the winter cold of Minnesota to prepare and to obtain in a pure form this salt by handling it nearly altogether in the outdoor cold. If a saturated water solution of the normal triammonium citrate, at room temperature, is added to alcohol, oily-like drops are obtained but no crystals. The water solution of the normal triammonium salt is slightly alkaline to rosolic acid (corallin), thus fulfilling the prediction of Hildebrand.[1] On exposure to the air a water solution of the salt loses ammonia and reacts acid. Upon prolonged heating on the steam bath or prolonged exposure to the air the solid salt loses ammonia and doubtless passes over into the diammonium citrate.

ANALYSIS OF THE TRIAMMONIUM CITRATE.

The carbon, hydrogen, and nitrogen contents were determined by elementary analyses of a sample of the salt that had been dried on the steam bath for an hour and then further dried over sulphuric acid in a desiccator for some days; 0.2501 gram of the salt gave:

(1) 0.1583 gram of water.
(2) 0.2712 gram of carbon dioxid.

Calculated for $(NH_4)_3C_6H_5O_7$	*Per cent*	Found *Per cent*
Hydrogen	7.05	7.04
Carbon	29.61	29.58

0.2115 gram of substance gave 0.0366 gram of nitrogen.
Nitrogen calculated for $(NH_4)_3C_6H_5O_7$, 17.28 per cent.
Nitrogen found, 17.30 per cent.

Assuming that the salt was pure triammonium citrate a tenth-normal solution was made and 50 cc. of this solution, corresponding to 0.4050 gram of the salt was taken for analysis. An excess of a standardized sodium hydroxid was added to this solution in a Kjeldahl flask and the ammonia was determined in the usual way; 0.88513 gram of ammonia was obtained. Ammonia calculated for $(NH_4)_3C_6H_5O_7$, 21.01 per cent; found, 21.02 per cent. The excess of alkali in the distillation flask was

[1] Loc. cit.

determined and the citric acid content of the salt found. Calculated citric acid for $(NH_4)_3C_6H_5O_7$, 78.98 per cent; citric acid found, 78.96 per cent.

For analysis and trial by a chemist in actual comparison with solutions in the daily determination of the phosphoric acid content of fertilizers a sample of the salt analyzed was sent to Paul Rudnick, of Armour and Company, Union Stock Yards, Chicago. His report is given below:

Rudnick: We made up a solution of ammonium citrate from the triammonium citrate which you sent us. The quantity received was a little more than sufficient for 500 cc. in all. Its reaction to azolitmin, by the method described in my paper "On the Preparation of Neutral Ammonium Citrate," was neutral. Analysis of the solution showed that the salt which you sent me must, therefore, have been 99.12 per cent pure triammonium citrate. The specific gravity of this solution was 1.0898 at 20° C. Accordingly we added the calculated additional amount of the salt, which made the specific gravity of the solution 1.092 at 20°C. The ratio between ammonia and citric acid was then that required by the Patten and Marti standard (J. Ind. Eng. Chem., 1913, **5**: 567).

We then prepared a solution of neutral ammonium citrate from pure citric acid and ammonia and analyzed four different samples of fertilizers with each of the two solutions. The results obtained were as follows:

Sample	Insoluble phosphoric acid: Solution triammonium citrate *Per cent*	Insoluble phosphoric acid: Official neutral ammonium citrate solution *Per cent*
10 and 5	0.74	0.71
Acid phosphate	0.10	0.10
Complete fertilizer containing acid phosphate only	2.29	2.27
Complete fertilizer containing acid phosphate and bone	4.55	4.58

The concordance of these results is all that could be expected.

REPORT ON NITROGEN.

By R. N. Brackett (Agricultural Experiment Station, Clemson College, S. C.), *Referee*, and H. D. Haskins (Agricultural Experiment Station, Amherst, Mass.), *Associate Referee.*

SELECTION OF SAMPLES.

After some correspondence with the associate referee and with C. H. Jones (Vermont) with regard to the nature of the samples to be sent out, and with Mr. Jones and J. P. Street (Connecticut) in reference to any possible modifications in their published methods of determining the activity of nitrogen in fertilizing materials and mixed fertilizers, nine samples were sent to the twenty laboratories consenting to take part in the work.

It may not be out of place to state why the particular materials selected this year were chosen, rather than some of the so-called "wet mix," or "base goods." It appeared to the referee that sufficient work had already been done both in the laboratory and in the field by Jones, Street, Haskins (Massachusetts), Frear (Pennsylvania), Hartwell (Rhode Island) and others to establish the fact that "wet mix" or "base goods" are acceptable as far as the activity of the nitrogen is concerned. On the other hand, there are on the markets, certainly in the South, and doubtless also to a very great extent in the North, very large quantities of leather preparations and so-called beet root manure, and smaller quantities of tartar pomace, or grape pomace, or grape fertilizer. The leather preparations masquerade under such terms as high grade tankage, tankage (and so far as I can learn are generally carried on the books of the fertilizer companies by these names), nitrogenous manure, (a very common name), nitrogenous material, organic manure, nitrolene, azotin, Munro's azotin, kanona tankage, Remsdorff tankage.

The special reason for selecting Samples 1, 2, and 3 was that work might be done on a mixture of tartar pomace and dried blood, the claim having been made that a mixture of these two materials in the proportion of nine of the former to one of the latter would not show a mean nitrogen activity by the Jones method. Special care was taken in the preparation of the samples and in securing a quantity large enough to meet all needs, even for pot tests, when desired.

OBJECT OF THE WORK.

As both the Jones and Street methods have been tried long enough to show that by the use of either of them, it is quite possible to differentiate between good and poor fertilizing materials, as a rule, and also to detect in mixed fertilizers the presence of poor or low grade materials, the chief object of the work this year has been to ascertain whether, with carefully prepared samples and explicit instructions, chemists in different laboratories would obtain reasonably concordant results, which would warrant the establishment of certain standards of nitrogen activity, if considered desirable, in raw materials and mixed fertilizers furnishing organic nitrogen.

INSTRUCTIONS FOR COLLABORATORS.

Samples are numbered 1 to 9, inclusive.

Samples 1 to 8, inclusive, are to be used for the so-called nitrogen availability determinations by the Jones and Street methods. They are raw materials with the exception of 4, which is a mixed fertilizer.

Sample 9 is a nitrate to be used for the determination of total nitrogen by the zinc-ferrous sulphate-soda method.

MODIFIED NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN (STREET).[1]

Weigh a quantity of the fertilizer, equivalent to 45 mg. of water-insoluble organic nitrogen,[2] on a moistened 11 cm. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add one gram sodium carbonate and 100 cc. of 2 per cent permanganate solution. Digest in a steam or hot-water bath for 30 minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of 10 minutes, At the end of the digestion remove from the bath, add 100 cc. of cold water, and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.

ALKALINE PERMANGANATE METHOD FOR ORGANIC NITROGEN ACTIVITY (JONES).[3]

(1) With mixed fertilizers:

(a) Transfer an amount of material equivalent to 50 mg. of water-insoluble organic nitrogen[4] to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When it is found necessary to use 4 or more grams of the original material to secure the 50 mg. of water-insoluble nitrogen, that is, when the percentage of water-insoluble nitrogen is 1.25 or less, weigh the required amount into a small beaker, wash by decantation, finally transfer to the filter and finish the extraction as previously directed. When a relatively large amount, that is, 7 to 10 grams of a fertilizer is to be extracted, it is desirable to weigh out duplicate portions. One is used for the determination of nitrogen activity by the alkaline permanganate method, and the other is Kjeldahled for its nitrogen content. Compare the latter figure with the result previously obtained from the 2 gram extraction (see second footnote) and in case of any marked discrepancy, that is, over 0.05 per cent of nitrogen, calculate the nitrogen activity on the basis of the exact nitrogen equivalent used.

(b) Dry the residue at a temperature not exceeding 80° C. and transfer from the filter to a 500 to 600 cc. Kjeldahl distillation flask (round-bottom preferred, but, if flat-bottom is used, incline at an angle of 30°). Add 20 cc. of water, 15 to 20 small glass beads to prevent bumping, and 100 cc. of alkaline permanganate solution (25 grams of pure potassium permanganate and 150 grams of sodium hydroxid, separately dissolved in water, the solutions cooled, mixed and made to volume of one liter.) Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly, below distillation point, with very low flame, using coarse wire gauze and asbestos paper between flask and flame, for at least 30 minutes. Gradually raise the temperature and when danger (if any) from

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[1] J. Ind. Eng. Chem., 1912, **4**: 438.

[2] Determined by washing one gram of the material on an 11 cm. filter with water at room temperature to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

[3] Vt. Agr. Exper. Sta., Bul. 173.

[4] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary.

frothing has ceased, distill until 95 cc. of distillate is obtained, and titrate as usual. In cases where a tendency to froth is noticed, lengthen the digestion period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. It is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation. The nitrogen thus obtained is the active water-insoluble organic nitrogen.

(2) With raw materials:

Transfer an amount of material equivalent to 50 mg. of water-insoluble organic nitrogen[1] to a small mortar, add about 2 grams of powdered rock phosphate, mix thoroughly, transfer to a filter and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When much oil or fat is present, it is well to wash somewhat with ether before extracting with water. Proceed as under (b) in (1).

(1) Follow these two methods as described.

(2) Make all determinations of nitrogen, total, water-insoluble, and permanganate-insoluble as follows: Place 0.5 gram (in the case of the water-insoluble, and of the permanganate-insoluble nitrogen, the residue, in which the nitrogen is to be determined) in a digestion flask; add 5 grams of potassium sulphate (powdered), 0.7 gram of mercuric oxid and 30 cc. of sulphuric acid (specific gravity 1.84). Place the flask over a low flame and heat below the boiling point until the solution is practically colorless, then raise the heat until solution boils sufficiently to condense and clean side and neck of flask. Do not keep at a high heat too long. After all adhering particles are washed down by the condensing acid, reduce the heat until contents of the flask boils gently, and continue the heat until clear and practically colorless. Time should not be over 2 hours. Dilute when cold, add potassium sulphid solution, and proceed with distillation as in the regular Kjeldahl process.

(3) Use acid and alkali of at least half strength for the titration of the ammonia from the permanganate-insoluble residue; that is, not more than half as strong as that used for total or for water-insoluble nitrogen, unless you are already using a tenth-normal alkali.

(4) Determine the so-called ammoniacal nitrogen by distilling a portion of each sample with magnesium oxid (Bur. Chem. Bul. 107, Rev., p. 9).

(5) Report results in per cent as follows:

Street method.	*Jones method.*
Total nitrogen	Total nitrogen
Ammoniacal nitrogen	Ammoniacal nitrogen
Water-insoluble organic nitrogen	Water-insoluble organic nitrogen
Permanganate-insoluble nitrogen	Nitrogen liberated by alkaline permanganate digestion.

TOTAL NITROGEN IN SAMPLE 9.

To 0.5 gram of the nitrate in 600 to 700 cc. flask add 200 cc. of distilled water, 5 grams of powdered zinc, from 1 to 2 grams of ferrous sulphate, and 50 cc. of a 36° Baumé soda solution. In the neck of the flask place some glass wool and connect with the distilling apparatus. Distill off the ammonia and collect as usual in tenth-normal sulphuric acid and titrate.

Determine moisture in all samples.

[1] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary.

RESULTS OF COLLABORATION.

As the results of the nitrogen determinations have been very discordant for the past few years, the precaution has been taken to give very explicit directions for the determination of nitrogen. It will be noted that it is the Kjeldahl-Gunning-Arnold method, which is prescribed for use in the nitrogen determinations.

LIST OF COLLABORATORS.

G. L. Davis, Agricultural Experiment Station, New Haven, Conn.
G. F. Anderson, Agricultural Experiment Station, Burlington, Vt.
J. J. Taylor, State Chemical Laboratory, Atlanta, Ga.
R. B. Deemer, Agricultural Experiment Station, Lafayette, Ind.
Wm. Rodes, Agricultural Experiment Station, Lexington, Ky.
E. R. Tobey, Agricultural Experiment Station, Orono, Me.
T. D. Jarrell and C. G. Remsberg, Agricultural Experiment Station, College Park, Md.
H. D. Haskins, Agricultural Experiment Station, Amherst, Mass.
O. F. Jensen, Agricultural Experiment Station, Lansing, Mich.
H. S. Chilton, Agricultural Experiment Station, Agricultural College, Miss.
E. E. Vanatta, Agricultural Experiment Station, Columbia, Mo.
Geo. E. Boltz, Agricultural Experiment Station, Wooster, Ohio.
J. H. Mitchell and B. F. Robertson, Chemical Department, Clemson College, S. C.
L. A. Hudgins, Agricultural Experiment Station, College Station, Tex.
J. H. Parkins, State Chemical Laboratory, Richmond, Va.
J. B. Robb, State Chemical Laboratory, Richmond, Va.

In making up these tables from the results as reported, it was found that E. E. Vanatta had given the figures for permanganate-soluble instead of permanganate-insoluble in the column headed Permanganate-insoluble, at least it appeared so, and the referee took the liberty of making the correction.

Attention should also be called to the fact that Parkins and Robb did not use the exact amount of material calculated from the water-insoluble organic nitrogen found, but very closely-approximating quantities, and they used the same amounts of each sample for both the Jones and Street methods.

COMMENTS OF COLLABORATORS.

G. L. Davis: Water determination a single one, while the total and ammonia nitrogen are averages of closely-agreeing duplicates. Methods outlined by referee were followed in all particulars.

J. J. Taylor: Much difficulty was experienced in getting agreeing duplicates by the Street method, especially with Sample 6. All results fairly concordant by Jones method, except with 1, 6 and 8 which, however, gave somewhat lower but concordant results when about 2 grams of ground phosphate rock were mixed with the sample before washing out the water-soluble nitrogen, as recommended by Jones

TABLE 1.

Comparative results on samples submitted for coöperation.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD: Nitrogen liberated by alkaline permanganate	JONES METHOD: Activity water-insoluble organic nitrogen	STREET METHOD: Permanganate insoluble organic nitrogen	STREET METHOD: Activity water-insoluble organic nitrogen
SAMPLE 1:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	
TARTAR POMACE								
G. L. Davis	6.40	2.52	0.10	2.45	0.91	37	0.82	66
G. F. Anderson	11.77	2.70	0.14	2.46	0.93	38	0.90	64
J. J. Taylor	12.26	3.07	0.17	2.71	0.83	31	1.20	56
R. B. Deemer	5.30	2.69	0.15	2.47	0.84	34	0.97	61
Wm. Rodes	14.06	2.72	0.10	2.64	0.79	30	1.15	56
E. R. Tobey	12.67	2.76	0.10	2.42	0.73	30	1.11	54
T. D. Jarrell and C. G. Remsburg	......	2.52	0.13	2.40	0.68	28	0.87	64
H. D. Haskins	14.14	2.48	0.10	2.38	0.90	38	0.83	65
O. F. Jensen	7.08	2.54	0.15	2.46	0.78	32	0.92	63
H. S. Chilton	9.50	2.46	0.15	2.41	0.92	38	0.79	67
E. E. Vanatta	12.13	2.50	0.12	2.41	1.08	45	1.14	53
G. E. Boltz	6.33	2.57	0.11	2.38	0.74	31	1.14	52
J. H. Mitchell	5.66	2.58	0.13	2.35	0.82	35	0.90	62
L. A. Hudgins	......	2.62	......	2.45	......	......	0.94	62
J. H. Parkins	......	2.70	......	2.55	0.96	38	1.10	57
J. B. Robb	......	2.70	......	2.58	0.86	33	0.96	63
SAMPLE 2:								
DRIED BLOOD								
G. L. Davis	15.60	12.60	0.19	12.11	9.21	76	0.93	92
G. F. Anderson	15.90	12.66	0.21	12.18	8.81	72	......	96
G. F. Anderson	......	......	......	12.32	......	......	0.49	96
J. J. Taylor	14.85	14.18	0.22	13.56	10.28	76	1.31	90
R. B. Deemer	14.86	12.82	0.25	12.01	9.40	78	0 99	92
Wm. Rodes	16.88	12.38	0.15	11.98	6.78	57	1 21	90
E. R. Tobey	16.13	12.30	0.16	11.73	8.63	74	3.91	67
T. D. Jarrell and C. G. Remsburg	......	12.41	0.23	11.89	5.33	45	0.86	93
H. D. Haskins	16.65	12.52	0.19	12.17	8.59	71	0.68	94
O. F. Jensen	16.32	12.52	0.21	12.15	8.86	73	1.07	91
H. S. Chilton	16.16	12.16	0.38	11.93	8.65	73	0.55	95
E. E. Vanatta	16.29	12.38	0.19	12.02	9.97	83	2.05	82
G. E. Boltz	16.21	12.57	0.20	12.21	8.00	66	1.10	91
J. H. Mitchell	16.60	12.65	0.21	11.76	9.31	79	0.99	92
L. A. Hudgins	15.21	12 65	......	12.21	......	......	1.10	91
J. H. Parkins	......	12.83	......	12.41	8.84	71	0.79	94
J. B. Robb	....	12.97	.....	12 31	9.32	76	2.03	83
SAMPLE 3:								
NINE BY WEIGHT TARTAR POMACE TO ONE DRIED BLOOD								
G. L. Davis	6.95	3.63	0.11	3.50	1.60	46	0.85	76
G. F. Anderson	12.06	3.64	0.14	3.51	1.61	46	......	......
G. F. Anderson	......	......	......	3.47	......	......	0.84	76
J. J. Taylor	12.70	4.18	0.18	3.78	1.54	41	1.29	66

TABLE 1—Continued.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD: Nitrogen liberated by alkaline permanganate	JONES METHOD: Activity water-insoluble organic nitrogen	STREET METHOD: Permanganate insoluble organic nitrogen	STREET METHOD: Activity water-insoluble organic nitrogen
SAMPLE 3:—Continued	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	
R. B. Deemer	5.70	3.85	0.18	3.41	1.40	41	1.12	67
Wm. Rodes	14.21	3.72	0.13	3.57	1.27	36	1.26	65
E. R. Tobey	11.31	3.40	0.10	3.32	1.26	38	2.00	40
T. D. Jarrell and C. G. Remsburg	......	3.49	0.14	3.34	1.09	33	1.04	69
H. D. Haskins	14.40	3.54	0.13	3.38	1.58	47	0.89	74
O. F. Jensen	10.74	3.64	0.14	3.48	1.72	40	0.96	72
H. S. Chilton	10.18	3.48	0.19	3.46	1.54	45	1.12	68
E. E. Vanatta	12.29	3.57	0.13	3.32	2.02	61	1.60	52
G. E. Boltz	7.56	3.63	0.12	3.43	1.27	37	1.52	56
J. H. Mitchell	6.91	3.60	0.13	3.32	1.32	40	0.96	71
L. A. Hudgins	......	......	......	3.52	......	......	0.49	86
J. H. Parkins	......	3.66	......	3.47	1.47	42	1.10	65
J. B. Robb	......	3.89	......	3.54	1.26	36	1.19	66
SAMPLE 4: MIXED FERTILIZER ABOUT 3.30 PER CENT NITROGEN (2 PER CENT FROM NITROGEN MANURE; 1 PER CENT FROM DRIED BLOOD AND 0.30 PER CENT FROM TARTAR POMACE)								
G. L. Davis	9.25	3.34	0.06	2.68	1.68	63	0.23	91
G. F. Anderson	10.52	3.43	0.09	2.81	1.78	63	......	......
G. F. Anderson	......	......	......	2.67	......	......	0.32	88
J. J. Taylor	9.25	3.74	0.14	3.04	2.01	66	0.38	87
R. B. Deemer	8.45	3.43	0.12	2.82	1.76	62	0.37	87
Wm. Rodes	10.86	3.41	0.10	3.05	1.53	50	0.52	82
E. R. Tobey	9.28	3.32	0.05	2.65	1.67	63	0.07	97
T. D. Jarrell and C. G. Remsburg	......	3.12	0.11	2.52	0.97	38	0.36	86
H. D. Haskins	11.82	3.30	0.11	2.80	1.78	63	0.34	88
O. F. Jensen	9.41	3.28	0.13	2.59	1.60	62	0.37	86
H. S. Chilton	9.59	3.22	0.13	2.49	1.46	59	0.40	84
E. E. Vanatta	10.58	3.29	0.09	2.59	1.80	69	0.76	71
G. E. Boltz	8.97	3.44	0.10	2.64	1.27	48	0.61	77
J. H. Mitchell	9.30	3.44	0.10	2.70	1.38	51	0.34	88
L. A. Hudgins	7.93	3.31	......	2.64	......	......	0.34	87
J. H. Parkins	......	3.48	......	2.97	1.94	65	0.32	89
J. B. Robb	......	3.66	......	3.02	1.67	55	0.46	84
SAMPLE 5: NITROGENOUS MANURE ABOUT 8 PER CENT NITROGEN								
G. L. Davis	8.78	8.31	0.18	6.52	4.11	63	0.57	90
G. F. Anderson	9.25	8.31	0.23	6.35	4.12	65	......	......
G. F. Anderson	......	......	......	6.38	......	......	0.75	88
J. J. Taylor	9.30	10.38	0.26	6.63	4.26	64	1.06	84
R. B. Deemer	8.02	8.30	0.23	6.17	3.97	64	1.07	83
Wm. Rodes	9.65	7.81	0.18	6.60	3.29	50	1.43	80
E. R. Tobey	8.79	8.00	0.16	6.28	3.72	59	0.36	94
T. D. Jarrell and C. G. Remsburg	......	8.08	0.23	6.16	2.41	39	0.76	87

TABLE 1—Continued.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD: Nitrogen liberated by alkaline permanganate	JONES METHOD: Activity water-insoluble organic nitrogen	STREET METHOD: Permanganate insoluble organic nitrogen	STREET METHOD: Activity water-insoluble organic nitrogen
SAMPLE 5:—Continued	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	
H. D. Haskins	10.28	8.12	0.22	6.70	4.26	63	0.71	89
O. F. Jensen	9.08	8.20	0.26	6.30	3.53	56	0.92	85
H. S. Chilton	9.22	8.08	0.25	6.38	3.82	60	0.85	87
E. E. Vanatta	8.78	8.00	0.20	6.11	4.49	73	1.01	83
G. E. Boltz	8.79	8.21	0.22	6.20	3.22	51	0.91	85
J. H. Mitchell	8.28	8.34	0.23	6.03	3.41	57	0.70	88
L. A. Hudgins	8.11	8.16	.....	6.26	......	......	1.00	84
J. H. Parkins	......	8.32	......	6.57	3.30	50	1.17	82
J. B. Robb	......	8.37	......	6.50	3.08	47	1.21	81
SAMPLE 6:								
NITROGENOUS MANURE ABOUT 6 PER CENT NITROGEN								
G. L. Davis	10.48	6.59	0.37	5.40	2.55	47	0.68	87
G. F. Anderson	11.03	6.63	0.39	4.79	2.42	51	......	......
G. F. Anderson	.....	.....	.....	4.81	......	.....	0.75	85
J. J. Taylor	10.55	7.25	0.42	5.16	1.94	38	1.25	76
R. B. Deemer	9.94	6.58	0.37	4.71	2.26	48	0.86	81
Wm. Rodes	11.42	6.43	0.33	5.22	2.12	41	1.31	75
E. R. Tobey	11.33	6.44	0.34	4.58	2.29	50	0.59	87
T. D. Jarrell and C. G. Remsburg	......	6.30	0.37	4.70	1.77	38	0.73	84
H. D. Haskins	11.81	6.54	0.39	5.36	3.36	62	0.83	85
O. F. Jensen	10.78	6.57	0.30	4.71	3.13	66	0.87	81
H. S. Chilton	10.85	6.34	0.38	5.73	2.24	39	0.73	87
E. E. Vanatta	10.69	6.47	0.36	4.85	2.79	57	1.39	71
G. E. Boltz	10.50	6.53	0.39	4.64	2.20	47	0.91	80
J. H. Mitchell	10.30	6.71	0.37	4.52	2.21	49	1.00	79
L. A. Hudgins	10.01	6.56	......	4.49	.....	.....	1.35	70
J. H. Parkins	......	6.76	......	5.24	2.49	48	1.09	79
J. B. Robb	......	6.72	.....	4.78	2.55	53	0.95	80
SAMPLE 7:								
BEET ROOT MANURE								
G. L. Davis	6.25	5.61	1.88	3.72	0.84	23	0.24	93
G. F. Anderson	8.17	5.72	1.93	3.58	0.79	22	......	......
G. F. Anderson	......	......	......	3.72	.....	.....	0.45	88
R. B. Deemer	6.31	5.75	1.93	3.47	0.77	22	0.56	83
Wm. Rodes	7.23	5.94	1.49	3.80	0.81	21	0.82	78
G. R. Tobey	7.11	5.54	1.80	3.50	0.76	22	0.31	91
T. D. Jarrell and C. G. Remsburg	......	5.45	1.77	3.58	0.99	28	0.56	84
H. D. Haskins	8.15	5.68	2.03	3.58	0.84	23	0.46	84
O. F. Jensen	6.57	5.64	1.80	3.62	0.83	23	0.48	86
H. S. Chilton	6.29	5.42	1.97	3.99	0.94	24	0.45	88
E. E. Vanatta	5.96	5.60	1.87	3.62	0.90	25	0.54	85
G. E. Boltz	6.70	5.70	1.94	3.65	0.68	19	0.62	83
J. H. Mitchell	6.38	5.67	1.80	3.43	0.75	22	0.57	83
L. A. Hudgins	...	6.12	......	3.52	.....	......	0.49	86
J. H. Parkins	......	5.83	......	3.79	0.93	23	0.55	85
J. B. Robb	...	5.74	...	3.65	0.97	26	0.53	85

TABLE 1—Concluded.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD: Nitrogen liberated by alkaline permanganate	JONES METHOD: Activity water-insoluble organic nitrogen	STREET METHOD: Permanganate insoluble organic nitrogen	STREET METHOD: Activity water-insoluble organic nitrogen
SAMPLE 8:	per cent	per cent	per cent	per cent	per cent		per cent	
BEET ROOT MANURE THREE PARTS BY WEIGHT TO NITROGENOUS MANURE ONE PART								
G. L. Davis	11.83	6.01	1.56	4.27	1.16	27	0.23	95
G. F. Anderson	13.47	6.11	1.60	4.25	1.18	28	.....	.....
G. F. Anderson	.....	.....	.....	4.28	.....	.....	0.76	82
J. J. Taylor	11.30	6.69	1.84	4.27	1.20	30	0.49	89
R. B. Deemer	10.82	6.16	1.55	4.06	2.06	50	0.61	85
Wm. Rodes	12.75	6.30	1.29	4.46	0.94	21	0.83	81
E. R. Tobey	12.40	5.78	1.56	4.20	1.13	27	0.21	95
T. D. Jarrell and C. G. Remsburg	.....	5.92	1.49	4.17	1.08	25	0.50	88
H. D. Haskins	13.22	6.06	1.76	4.24	1.15	27	0.33	92
O. F. Jensen	11.95	6.04	1.60	4.14	1.10	26	0.38	90
H. S. Chilton	11.87	5.80	1.75	4.27	1.65	38	0.40	91
E. E. Vanatta	12.12	5.95	1.57	4.05	1.45	35	0.59	85
G. E. Boltz	11.81	6.07	1.58	4.24	1.02	24	0.75	82
J. H. Mitchell	11.64	5.95	1.62	3.99	1.00	25	0.37	91
L. A. Hudgins	11.15	6.50	.....	4.16	.....	.....	0.62	85
J. H. Parkins	.....	6.14	.....	4.29	1.29	29	0.40	90
J. B. Robb	.....	6.18	.....	4.20	1.23	29	0.37	91

TABLE 2.

Summary: Samples Nos. 1 to 8 inclusive.

SAMPLE NUMBER	JONES METHOD: Reported	JONES METHOD: Per cent good	STREET METHOD: Reported	STREET METHOD: Per cent good
1	15	87	16	81
2	15	73	16	81
3	15	60	16	31
4	15	60	16	75
5	15	40	16	75
6	15	60	16	75
7	14	100	15	87
8	15	73	16	88
Average	....	69	....	74

TABLE 3.

Sample 9: Nitrate of soda, commercial.

ANALYST	MOISTURE	TOTAL NITROGEN AVERAGE	RESULTS RECEIVED
G. L. Davis	1.95	15.44	15.44, 15.42, 15.46
G. F. Anderson	1.11	15.38	....
R. B. Deemer (?)	0.25	15.70	....
J. J. Taylor	1.40	15.55	15.72, 15.80, 15.58
Wm. Rodes	1.56	15.29	15.28, 15.30
E. R. Tobey	1.24	15.92	....
H. D. Haskins	....	15.56	....
O. F. Jensen	....	15.47	15.44, 15.49
H. S. Chilton	2.06	15.71	....
E. E. Vanatta	1.43	14.85	14.96, 14.76, 14.83
G. E. Boltz	1.05	14.89	14.84, 14.88, 14.92, 14.95
B. F. Robertson	2.35	15.30	....
J. H. Parkins	....	15.58	15.54, 15.89, 15.48, 15.40

for raw materials. Commenting on Sample 9—in my opinion this (the zinc-ferrous sulphate-soda) method is the best method for nitrates. I further believe that more accurate results could be obtained by weighing a larger quantity, say 5 to 7 grams, of the sample into a 250 cc. flask, making up solution and taking out an aliquot. This would tend to lessen the manipulative error in weighing out such a small quantity of material.

R. B. Deemer: Instructions were followed as requested with the exception of a variation in the usual method of titration in the determination of ammoniacal nitrogen on Samples 7 and 8. In the method of digestion the amount of acid greatly prolongs the time required for distillation of the ammonia, owing to the fact that the alkali necessary to neutralize this acid fills the flask so as to produce frothing unless distilled very slowly. With the digestion carried on at such a low temperature and for a period of only 2 hours, 20 cc. would be sufficient and not make this delay. The percentage of water-insoluble nitrogen obtained on 1 gram of material is slightly higher than that obtained on 2 grams. The filtrate from the neutral permanganate digestion of Samples 6 showed no excess of the reagent; the effect, if any, is not evident in the results.

A careful study of the results obtained by the Street and Jones methods shows practically no advantage of one over the other so far as accuracy of results is concerned. The latter is the shorter in point of time, and generally speaking is the easier of manipulation. The most serious objection to this method is the distillation of 95 cc. from such a small volume, which necessitates carrying the contents of the flask practically to dryness, causing caking and a large percentage of breakage. This probably does not occur with some forms of condensers. From some results obtained it appears that the success of this method depends upon the completion of the distillation of the required volume of the distillate in the time specified. The most serious difficulty presented by the Street method is the time required for the washing of the residue from the permanganate digestion. This washing might be hastened by the selection of a grade of filter paper specially suited to this work, but as the method is not specific in this particular a C. S. & S. No. 588 folded filter was used and may account for the slow filtration.

T. D. Jarrell: The distillates from Samples 7 and 8 in the determination of the ammoniacal nitrogen were very cloudy, the cloudiness beginning when about 40 cc. of the distillate had come over, but the sharpness of the titration did not appear

to be interfered with thereby. In every determination by the Street method, 1 and 6 decolorized all the permanganate solution used.

O. F. Jensen: When Samples 7 and 8 are washed on a filter and the ammonia determined in the washings, the results are about 0.3 per cent lower than the results by distillation with the samples in a flask. Results on 9 by the Ulsch method for comparison with the zinc-ferrous sulphate-soda method: 15.64 and 15.70, as against 15.44 and 15.49; the Ulsch method giving about 0.20 per cent higher results.

G. E. Boltz: One of the greatest sources of error by either method seems to be in transferring from the filter paper, in case of the Street method, the water-insoluble residue to the beaker, and in the Jones method, the dried residue to the Kjeldahl flask. Is there any reason why an additional amount of permanganate cannot be used to oxidize the filter paper, so that the filter paper can be transferred with the residue, or an abestos filter be used which could be transferred with the residue?

J. H. Mitchell: I believe that a careful analyst can get fairly good results with either method, although occasionally results obtained in two determinations run side by side will fail to check by five to ten points. The Jones method is much shorter. In this method there is some difficulty in transferring sample from filter paper to distillation flask, as it is hard to remove all the residue from the paper.

B. F. Robertson: The only advantage of the zinc-ferrous sulphate-soda method over the combination method,[1] is the rapidity of the determination, when only a few determinations are to be made. Too close attention is required where a great amount of work is carried on at the same time, for this method to be satisfactory; and, too, more experience is required in order to obtain correct results than a method for routine work should demand.

L. A. Hudgins: Not satisfied with results on Samples 3, 6, and 7 by the Street method. Results by the Jones method were not regarded as accurate and were not reported.

J. H. Parkins: By the Street method with Samples 1, 5, and 6 the permanganate solution was completely decolorized, and 3 partly so.

DISCUSSION OF RESULTS.

JONES AND STREET METHODS FOR NITROGEN ACTIVITY.

Sample 1.—At first glance the most striking thing about Table 1 is the very wide variation in the moisture reported, which, however, seems to bear little or no relation to the total nitrogen figures. The figures for total nitrogen are, with the exception of the Taylor result, quite satisfactory, and the same can be said of the water-insoluble organic nitrogen results, as well as for those on ammonia nitrogen. With the exception of the determinations by Jarrell and Vanatta, the results reported for nitrogen activity by the Jones method are on the whole satisfactory. The same may be said of the results reported by the Street method, if the results by Tobey, Vanatta, and Boltz are excepted.

Sample 2.—The moistures here are much more uniform. With the exception of the results by Taylor and Chilton, the total nitrogen results are fairly satisfactory. The same may be said of the ammonia nitrogen

[1] Bur. Chem. Bul. 107, Rev., p. 8—Gunning method modified for nitrates, with addition of mercury oxid; or Kjeldahl-Gunning-Arnold modified for nitrates.

figures, if those of Chilton are excepted. The water-insoluble organic nitrogen results are a little disappointing. With the exception of the results reported by Rodes, Jarrell, Vanatta, and Boltz, the figures for nitrogen activity by the Jones method are satisfactory; and the same may be said of the Street method, if the results of Tobey, Vanatta and Robb are omitted.

Sample 3.—The moisture determinations are again remarkable and bear no definite relation to the total nitrogen. With the exception of the results of Taylor, the figures for total nitrogen may be regarded as fairly satisfactory. The ammonia nitrogen results are quite so, and the water-insoluble organic nitrogen figures are highly satisfactory, with the possible exception of those of Taylor again. About nine of the results by the Jones method, varying from 40 to 46 per cent, show a fair agreement; five below 40 per cent are obviously too low, and one 61 per cent much too high. These nine best, and probably the most correct, of the results show that a mixture of nine parts by weight of tartar pomace and one of dried blood will give a mean nitrogen activity by the Jones method. The results by the Street method are still more variable, five being from 71 to 76 per cent, seven from 65 to 69 per cent, and four scattering—52, 56, 40, and 86 respectively. Seven of these results show that by the Street method a mean nitrogen activity is given when a mixture like Sample 3 is made.

Sample 4.—While the moisture results are more uniform, they are still too variable. The total nitrogen figures are again fairly satisfactory, with the exception of Taylor and Robb. The ammonia nitrogen figures are on the whole satisfactory. The water-insoluble organic nitrogen results are somewhat too variable. About nine of the results by the Jones method show a reasonable agreement, the remainder, below 60 per cent, appear to be too low. About twelve of the results by the Street method show a fair agreement, the rest with one exception appear too low.

Sample 5.—The moisture and total nitrogen results are again rather variable and bear no definite relationship to one another. The ammonia nitrogen figures are good, and the water-insoluble organic nitrogen figures on the whole good. By the Jones method six results are from 60 to 65 per cent, six from 50 to 59 per cent, and the remaining three 39, 47, and 73 per cent, respectively. The results by the Street method are much more satisfactory, eight being from 85 to 90 per cent, seven from 80 to 84 per cent, and one, 94 per cent.

Sample 6.—The moisture and the total nitrogen results leave something to be desired. The ammonia nitrogen results are excellent, while those on water-insoluble organic nitrogen are too variable again. With the exception of the results of Taylor, Rodes, Jarrell, Haskins, Jensen, and Chilton, the remaining nine results by the Jones method may be

considered to agree fairly well, if Jones' result is taken as a criterion, which seems justified. Twelve results by the Street method, varying from 79 to 87 per cent, show a reasonable agreement, while the remaining six results, from 70 to 76 per cent appear to be low.

Sample 7.—The moisture figures are too variable. The total nitrogen results are, with the exception of those of Hudgins, quite satisfactory, and so on the whole are the ammonia nitrogen results, as well as the water-insoluble organic nitrogen results. The fourteen results reported by the Jones method are highly satisfactory and agree well. Thirteen of the results by the Street method are in good agreement, while the Davis result is a little high and the Rodes result too low.

Sample 8.—The moisture figures are better. The total nitrogen figures are, with the exception of those of Taylor and Hudgins, very satisfactory. The ammonia nitrogen results are on the whole good. The water-insoluble organic nitrogen figures are fairly good. About eleven of the results by the Jones method are in fair agreement, while the results reported by Deemer, Chilton, and Vanatta are too high and that by Rodes too low, as compared with the rest. The results by the Street method are more uniform and in better agreement, with the exception of those of Davis and Tobey, which appear too high.

ZINC-FERROUS SULPHATE-SODA METHOD.

Sample 9.—Though a considerable variation in moisture results is apparent, there does not seem to be any reasonable relationship between them and the total nitrogen figures; they do not follow the same curve, and, furthermore, the moisture is so small that these figures may be neglected in the discussion. A discrepancy of over 1 per cent exists between the highest and lowest nitrogen results reported in the table. If the Tobey and the Vanatta and Boltz results are omitted as being obviously too high and too low, respectively, as compared with the remaining ten results, then these ten results fall into two groups of five each: (a) 15.55 to 15.71, average 15.62; (b) 15.29 to 15.47, average 15.38. These averages differ 0.24 per cent, while, if group (a) or (b) be considered alone, the results are quite favorable to the method; when all the results are taken into account, it appears that more work is necessary before recommending the method as official, and that the comments of Robertson are fully justified.

CONCLUSIONS.

(1) The referee should have given specific directions for determining moisture, as no doubt at least part of the differences reported are due to different conditions, resulting from various forms of baths used. It is

rather interesting to note that the greatest variations in the moisture figures occur in the samples containing tartar pomace.

(2) Previous experience that both the Jones and the Street methods enable one to differentiate between good and poor organic nitrogenous materials is confirmed. An exception is to be noted in the case of Sample 7, beet root manure. It is interesting to note further that in pot tests made by Jones, he obtained results which agree with the low activity shown by his method for this material. This is a confirmation of the previous work of Jones and Hartwell, which indicates that the Jones method gives results more in accordance with pot tests than the Street method.

(3) The testimony of the collaborators is that the Jones method is somewhat shorter, but the work reported certainly shows that in the hands of the inexperienced more uniform results and more closely-agreeing results are obtained by the Street than by the Jones method. The indications are that more experience is required to carry out the Jones method accurately, and that, therefore, there is a larger personal equation.

(4) The results this year, while somewhat disappointing, indicate the possibility of fixing standards of activity, if so desired. The results on Sample 4, confirm the standard for mixed fertilizers recommended in South Carolina, which standard was based on the examination of 1536 mixed fertilizers. The South Carolina standard recommended is, that if the water-insoluble organic nitrogen amounts to as much as one-third of the total nitrogen, this water-insoluble organic nitrogen must show an activity of 75 per cent by the Street method.

KJELDAHL-GUNNING-ARNOLD METHOD.

By oversight the referee did not send out a special sample for this work. This method was adopted as official by this association in 1908 but has never been published in the Methods of Analysis, as Bulletin 107, Revised, has not been revised since that time. The nitrogens in Samples 1 to 8, inclusive, were determined by this method. An examination of the results for total nitrogen will show the agreement of results obtained by sixteen different analysts, which with the exception of those on Sample 2 are quite satisfactory.

As was to be expected Samples 1 and 2, containing respectively the smallest and the largest amounts of nitrogen, show the least and the greatest difference and the greatest and least average difference. On the whole the results are very satisfactory and indicate that this method gives very closely-agreeing results in the hands of different chemists. As no sample was sent out specially for this work, we have no comparative results to submit by other methods for determining nitrogen, but the

TABLE 4.

Total nitrogens by Kjeldahl-Gunning-Arnold method.

SAMPLE	RESULTS REPORTED	GREATEST DIFFERENCE	AVERAGE DIFFERENCE	REMARKS
1	15	0.30	0.144	Omitting results by Taylor.
2	14	0.67	0.260	Omitting results by Taylor and Chilton.
3	14	0.49	0.224	Omitting results by Taylor.
4	14	0.36	0.223	Omitting results by Taylor and Robb.
5	14	0.37	0.200	Omitting results by Taylor and Rodes.
6	15	0.46	0.244	Omitting results by Taylor.
7	13	0.41	0.222	Omitting results by Hudgins and Rodes.
8	13	0.40	0.233	Omitting results by Taylor, Hudgins and Rodes.
Totals.....	112	3.46	1.780	
Averages..	....	0.308	0.159	

results in our own laboratory and those given by Mr. Trescot show that this method is to be preferred to any other for rapid and accurate work, unless further investigation shall show that the substitution of copper sulphate for oxid of mercury gives as good or better results. Last January I received a letter from A. J. Patten (Michigan), who offered to let me have the results of some recent work done in his laboratory on the Kjeldahl-Gunning-Arnold method with the use of copper sulphate in lieu of oxid of mercury. These results are given here:

TABLE 5.

Determination of nitrogen by the Gunning-Copper and Kjeldahl-Gunning-Arnold methods (Patten).

SUBSTANCE	GUNNING-COPPER METHOD $1\frac{1}{2}$ HOURS			KJELDAHL-GUNNING-ARNOLD METHOD $1\frac{1}{2}$ HOURS		
	Maximum	Minimum	Average	Maximum	Minimum	Average
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Gelatin..................	15.14	15.12	15.13	15.16	15.04	15.09
Egg albumin (dried).....	12.86	12.75	12.80	12.86	12.80	12.83
Peptone..................	14.49	14.38	14.45	14.49	14.38	14.43
Casein...................	13.87	13.81	13.83	13.92	13.81	13.85
Feathers.................	14.49	14.43	14.47	14.54	14.38	[1]14.46
Leather..................	4.83	4.72	4.76	4.80	4.75	4.78
Fish scrap...............	6.48	6.35	6.43	6.51	6.43	6.47
Animal tankage..........	6.32	6.26	6.31	6.35	6.29	6.33
Garbage tankage.........	2.99	2.96	2.98	3.00	2.96	2.99
Beef scraps..............	9.14	8.97	9.04	9.05	8.97	8.99
Castor bean pomace......	4.66	4.55	4.59	4.55	4.52	4.53
Cocoa....................	4.01	3.94	3.97	3.97	3.90	3.93
Cottonseed meal.........	7.33	7.30	7.31	7.29	7.24	7.26
Cottonseed meal.........	6.43	6.40	6.42	6.37	6.32	6.35
Linseed meal............	5.64	5.59	5.61	5.50	5.50	5.50
Silage...................	1.30	1.26	1.28	1.29	1.26	1.27
Flour....................	2.43	2.41	2.42	2.44	2.43	2.43
Bran.....................	2.60	2.55	2.58	2.58	2.58	[1]2.58
Bone meal...............	3.06	3.02	3.04	3.11	3.02	3.07
Peat.....................	2.41	2.37	2.38	2.37	2.36	2.37

[1] Two determinations only.

TABLE 6.

Comparative study of time of digestion by the Gunning-Copper and Kjeldahl-Gunning-Arnold methods (Patten).

SAMPLE AND METHOD	1 HOUR				1½ HOURS			
	Determination	Maximum	Minimum	Average	Determination	Maximum	Minimum	Average
		per cent	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*
BONE MEAL:								
Gunning-Copper	6	2.18	2.16	2.16	4	2.20	2.18	2.19
Kjeldahl-Gunning-Arnold	6	2.25	2.19	2.20	4	2.20	2.18	2.19
DRIED BLOOD:								
Gunning-Copper	6	14.11	14.03	14.07	6	14.24	14.07	14.13
Kjeldahl-Gunning-Arnold	6	14.32	14.11	14.24	6	14.32	14.19	14.29
CYANAMID:								
Gunning-Copper	6	15.75	15.37	15.52	6	15.62	15.50	15.53
Kjeldahl-Gunning-Arnold	6	15.62	15.46	15.55	6	15.54	15.41	15.49
LINSEED MEAL:								
Gunning-Copper	6	5.53	5.45	5.49	5	5.62	5.50	5.57
Kjeldahl-Gunning-Arnold	6	5.62	5.53	5.56	4	5.62	5.59	5.61
	2 HOURS				3 HOURS			
BONE MEAL:								
Gunning-Copper	6	2.20	2.18	2.19	6	2.23	2.20	2.20
Kjeldahl-Gunning-Arnold	6	2.23	2.19	2.20	6	2.22	2.20	2.20
DRIED BLOOD:								
Gunning-Copper	6	14.32	14.15	14.22	6	14.40	14.23	14.29
Kjeldahl-Gunning-Arnold	6	14.30	14.19	14.25	6	14.34	14.15	14.26
CYANAMID:								
Gunning-Copper	6	15.67	15.46	15.55	6	15.58	15.50	15.53
Kjeldahl-Gunning-Arnold	5	15.62	15.50	15.55	6	15.62	15.50	15.55
LINSEED MEAL:								
Gunning-Copper	6	5.62	5.50	5.55	6	5.56	5.64	5.62
Kjeldahl-Gunning-Arnold	6	5.59	5.53	5.58	6	5.62	5.56	5.58

An examination of the figures given in these two tables shows that the results are very satisfactory and leave little or nothing to be desired either as to accuracy or time of digestion.

B. F. Robertson of my own laboratory (Clemson College, S. C.) has been doing some work recently and reports as follows:

> I have used the Kjeldahl-Gunning-Arnold method for total nitrogen since 1908, and regard this method as the most satisfactory that has yet been brought out, the only objection being the use of mercury, which fouls the condensing tubes in the distillation. Recently I have made some determinations using copper sulphate instead of mercury, and find this to be satisfactory, but requiring a little more time for the digestion. On 21 samples with nitrogen content varying from 2 to 15 per cent, the general average was 0.03 per cent higher than when mercury was used. With only this limited amount of work, I am unable to say whether copper sulphate can be used with as much accuracy under all conditions as mercury.

It may not be out of place in this connection to call attention to the work of T. C. Trescot, Chief of the Nitrogen Laboratory, Bureau of Chem-

istry, published in the Journal of Industrial and Engineering Chemistry, 1914, volume 5, page 914, "Comparison of the Kjeldahl-Gunning-Arnold Method with the Official Kjeldahl and the Official Gunning Methods of Determining Nitrogen." Mr. Trescot closes his paper as follows:

> The general conclusion from these results is that the Kjeldahl-Gunning-Arnold method with one and one-half hours' oxidation, except in the case of cyanamids, which require two and one-half hours, gives more concordant and reliable estimations of nitrogen than the official Gunning or the official Kjeldahl methods, both of which require from 3 to 4 hours for oxidation, depending upon material.

I understand from his paper that Mr. Trescot used mercury and no copper sulphate.

RECOMMENDATIONS.

It is recommended—

(1) That the zinc-ferrous sulphate-soda method for nitrates be further studied during the coming year, with a view of final adoption as official in 1916, and that it be now adopted as provisional.

(2) That the Jones and Street methods for the determination of organic nitrogen activity be further studied during the coming year, with the special purpose in view of improving or modifying the manipulations in the conduct of each process, so as to increase the accuracy of the water-insoluble organic nitrogen determinations, and, in the case of the Jones method, to overcome the difficulties experienced by most analysts in the distillation with alkaline permanganate; and that they be now adopted as official.

(3) That the Kjeldahl-Gunning-Arnold method be further studied, although already adopted as official, especially as to the use of copper sulphate in place of mercury.

No report was made by the associate referee on the special study of the Kjeldahl method.

ANALYSIS OF NITROGEN IN LEATHER WASTE.

By R. Phillips Rose (Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.).[1]

During the past few months the Mellon Institute of Industrial Research has been conducting quite an extensive research on new methods of converting leather waste into fertilizer using the alkaline and neutral permanganate methods for the determination of available organic nitro-

[1] Not read at the meeting.

gen for control of the work. Since some very interesting data in regard to the application of the two methods of analysis have been obtained, it was thought that perhaps this information would be of interest to the referee of the work on nitrogen done in connection with the work of the Association of Official Agricultural Chemists.

In carrying out some 400 analyses of treated leather for available organic nitrogen, it was noticed that there occurred quite wide variations in the results obtained by the use of the two methods. The neutral permanganate method in all cases gave constant results, but the alkaline permanganate in every case gave lower results than the neutral and there was also a variation between results obtained at different times using the alkaline method on the same sample, although there was always good agreement between duplicates. In using both methods the directions for the work described in Bulletin 162 of the Bureau of Chemistry were followed rigidly and every precaution taken to insure accuracy.

In the beginning it was thought that this variation was due to oxidation of the ammonia in the distillation with alkaline permanganate; accordingly, a series of experiments was carried out to test this point, but in every case negative results were obtained. This result was rather surprising when the work of Herschkowitsch (*Zts. physikal. Chem.*, 1908–09, **65**: 93) is considered.

Since it is a well-established fact that ammonia forms complex compounds with some manganese salts the next step was to test this supposition, and it was found that amounts of ammonia up to 14 per cent of the total content of nitrogen were retained by the residue. The method of obtaining the results, which are given, is as follows: The soluble part of the residue remaining after the distillation of the fertilizer with the alkaline permanganate solution (25 grams of potassium permanganate plus 150 grams of sodium hydroxid per liter) was taken up with 100 cc. of distilled water, a little cane sugar added to destroy any potassium permanganate remaining in the solution, potassium sulphid added to precipitate any soluble manganese compounds and the resulting mixture distilled, the ammonia being collected in standard acid. The results were checked by the neutral permanganate method and by reversing the alkaline permanganate method, that is, by digesting the material with the alkaline permanganate solution on a water bath for one hour, filtering through an asbestos mat in a Gooch crucible, washing the residue with distilled water and analyzing the residue for nitrogen by the Gunning modification of the Kjeldahl method for total nitrogen. The results are shown in the following table.

These analyses were made in duplicate, no duplicates being accepted that did not agree within 0.2 per cent. All reagents were checked for nitrogen and the results corrected accordingly. Nos. 1 to 3 inclusive

FERTILIZER	TOTAL NITROGEN	TOTAL NITROGEN AVAILABLE BY ALKALINE POTASSIUM PERMANGANATE	TOTAL NITROGEN IN RESIDUE	TOTAL AVAILABLE NITROGEN
	per cent	*per cent*	*per cent*	*per cent*
No. 1	10.21	48.51	14.59	63.10
Same checked by neutral potassium permanganate method				63.17
Same checked by reverse alkaline potassium permanganate method				63.21
No. 2	9.87	89.05	9.03	98.08
Same checked by neutral potassium permanganate method				98.13
Same checked by reverse alkaline potassium permanganate method				98.17
No. 3	9.53	81.47	4.51	85.98
Same checked by neutral potassium permanganate method				86.18
Same checked by reverse alkaline potassium permanganate method				86.23
No. 4	5.34	76.53	6.87	83.40
Same checked by neutral potassium permanganate method				83.27
Same checked by reverse alkaline potassium permanganate method				83.43

were samples of treated leather, while No. 4 was a sample of packing-house tankage.

This work is being continued as rapidly as possible and will be published when completed. On account of the conclusiveness of all results (of which these are only selections made at random) I thought it advisable to make this report to you in order that it be brought before the committee on nitrogen of the association.

REPORT ON AVAILABILITY OF POTASH.

By E. E. Vanatta (Agricultural Experiment Station, Columbia, Mo.), *Referee.*[1]

At the beginning of this year the referee, in coöperation with M. F. Miller of the Soils Department and P. F. Trowbridge of the Agricultural Chemistry Department of the University of Missouri, planned a series of pot cultures to study the effect of different soil treatments on the availability of potash, using quartz sand and finely-ground feldspathic rock as a carrier of insoluble potash, said availability to be measured by plant growth supplemented by chemical determinations.

A copy of the plan was mailed to each of the chemists who had consented to coöperate in this work. R. Harcourt of Guelph, Canada, who

[1] Read by P. F. Trowbridge.

offered some valuable suggestions, was the only collaborator who was in position to take up this work. No report on the results of his work has been received as yet.

The Soils Department of the Missouri Agricultural Experiment Station took charge of the pot experiment. Seven series, three each, using three-gallon pots, were prepared. Two pots of each series were planted with corn, the other being left as a check. Sterile quartz sand was used at the base. To all of the pots optimum amounts of nitrogen, phosphorus, magnesium, and chlorin were added, sufficient for the growth of the corn plants. Series 1 was used as the check. Series 2 received in addition calcium oxid at the rate of 3,000 pounds per acre, and sufficient finely-ground feldspar to make a soil of 2 per cent potash. Series 3 received limestone at the rate of 4,500 pounds per acre with the same amount of feldspar as in Series 2. Series 4 received the feldspar as in Series 2 and finely-cut blue grass at the rate of 15 tons of fresh grass per acre. Series 5 received the feldspar and starch at the rate of 5 tons per acre. Series 6 received the feldspar which had been heated at 100°C. for 5 hours. Series 7 received the finely-ground feldspar.

The feldspar used in this experiment contained 13.40 per cent potash. Later experiments showed that this rock contained 0.044 per cent potash soluble in distilled water.

All of the pots were given the same treatment for moisture, optimum condition being attempted. The finely-ground feldspar with the sand showed a strong tendency to bake and the corn plants failed to thrive. The only plants which appeared to be normal were those in the check pots which contained no feldspar. The cultures were all discarded and a second series prepared duplicating the first, except that only one-third as much feldspar was used. These cultures have not been growing long enough to complete the test, but the present condition indicates a probable beneficial use of the feldspar in connection with the green blue grass. The pots containing the feldspar which had been heated appear next favorable in condition. The pots treated with limestone and the pots containing the untreated feldspar appear to be no better than the pots to which no feldspar had been added. The pots containing starch and those to which lime had been added have less growth than the check pots. This experiment will be continued for another year.

REPORT ON DETERMINATION OF POTASH.

By T. D. Jarrell (Agricultural Experiment Station, College Park, Md.), *Associate Referee.*

The work on the determination of potash for this year has included coöperative tests of (1) the use of denatured alcohol for washing potassium chloroplatinate, with special reference to the denaturing agents, (2) the necessity for the use of hydrochloric acid in the water extract, and (3) the perchlorate method. Sixteen chemists expressed a desire to coöperate in this work, and reports were received from ten, including the report of the associate referee. Three samples were sent out to each chemist requesting them: Sample 1: commercial muriate of potash; Sample 2: kainit; and Sample 3: a mixture of kainit and acid phosphate.

INSTRUCTIONS TO COLLABORATORS.

SAMPLES 1 AND 2.

Determine potash by (a) official method, and (b) perchlorate method. For Sample 1, use 1.25 grams for a 250 cc. flask or 2.50 grams for a 500 cc. flask and use 50 cc. aliquot for each determination corresponding to 0.25 gram charge. For Sample 2, use 2.50 grams for a 250 cc. flask or 5 grams for a 500 cc. flask and take 50 cc. aliquot for each determination corresponding to 0.50 gram charge.

Perchlorate method.—Dissolve the potash as in the official method, using the quantity as directed in the preceding paragraph. While hot, add barium chlorid solution, drop by drop, in slight excess with constant shaking (12 grams of barium chlorid dissolved in 95 cc. of water and 5 cc. of concentrated hydrochloric acid). Cool, make to mark and shake. Filter, and transfer 50 cc. of the solution to an evaporating dish, preferably of platinum, add 5 cc. of perchloric acid, evaporate on steam bath with occasional stirring until it becomes thick. Take up with hot water, add 5 cc. more of perchloric acid and evaporate to dryness with occasional stirring (the stirring may be carried on by rotating the dish with fingers). Then heat the residue carefully on a hot plate until all free hydrochloric acid is driven off and dense, white fumes of perchloric acid appear. Cool, add 20 cc. of strong alcohol saturated at working temperature with potassium perchlorate. Stir well and filter through a prepared Gooch crucible, wash with about 20 cc. of the alcohol wash and finally with 20 cc. of a mixture of equal parts of strong alcohol and ether; dry to constant weight at not over 120°C. and weigh.

Factor for converting potassium perchlorate to potash, 0.34.

(Modification of German Kali Syndicate method. See *J. Amer. Chem. Soc.*, 1899, **21**: 33, *Mining and Engineering World*, 1912, **36**: 605-606.)

SAMPLE 3.

Determine potash by (a) official method, using the method of making up solutions as adopted by the association in 1912 (Bur. Chem. Bul. 152, p. 41), (b) modified official method, and (c) perchlorate method.

Modified official method.—This is the official method omitting the addition of 2 cc. of concentrated hydrochloric acid and boiling. After washing 2.50 grams on a

$12\frac{1}{2}$ cm. filter paper into a 250 cc. graduated flask with 200 cc. of boiling water, add directly ammonium hydroxid and ammonium oxalate and proceed as in the official method.

Perchlorate method.—Proceed as in the official method until after the addition of 1 cc. of 1 to 1 sulphuric acid and ignition. Dissolve residue in about 25 cc. of hot water, add barium chlorid solution in slight excess, made up as already described; filter into evaporating dish, wash the precipitate and filter paper with hot water. Add 5 cc. of perchloric acid to filtrate, evaporate on steam bath with occasional stirring by rotating the dish with fingers, until thick. Take up with hot water, add 5 cc. more perchloric acid, evaporate to dryness with occasional stirring. Heat the residue carefully on hot plate until free hydrochloric acid is driven off and dense white fumes of perchloric acid appear. Cool, add the alcohol wash; stir, filter, and wash, dry and weigh as described for Samples 1 and 2.

Test also the use of denatured alcohol for washing potassium chloroplatinate. Wash a precipitate of potassium chloroplatinate alternately with 80 per cent ethyl alcohol and denatured alcohol using 50 cc. for each wash. Please report the denaturing agents in the denatured alcohol.

It is requested also that you test thoroughly the modified official method, that is, the necessity for the addition of hydrochloric acid, on some of your own samples. There seems to be some doubt as to the necessity of adding hydrochloric acid to the potash solution; therefore, I desire to have as full a report on this phase as possible.

Notes on perchlorate method.—Potash, etc., must be in the form of chlorids. The stirring and redissolving the solution after addition of perchloric acid greatly assist the removal of other salts later. Surr[1] stated that the excess of barium chlorid does no harm, as the barium perchlorate which is afterward formed is readily soluble in alcohol. Hence, the necessity for the addition of an excess of perchloric acid. Should high results be secured, test your potassium perchlorate precipitate for the presence of barium. The trouble may be caused by not adding enough perchloric acid to change the excess of barium chlorid originally added to barium perchlorate. If that should be the case, barium chlorid would be weighed with the potassium perchlorate. Barium chlorid is but slightly soluble in alcohol. A large excess of barium chlorid should be avoided; 10 cc. of perchloric acid seems to be sufficent for these samples. The perchloric acid available is generally of specific gravity, 1.12, and contains about 20 per cent acid.

RESULTS OF COLLABORATION.

A comparison of results by the official, the modified official (hydrochloric acid omitted from potash solution), the official using denatured alcohol, and the perchlorate methods, is given in the following table.

COMMENTS OF ANALYSTS.

O. B. Winter: The results on Samples 2 and 3 are fairly satisfactory, but those on 1 are not. On Sample 1, I could not get good results by any method; the fou r results reported by the official method are those nearest one another and somewhere near the average. I do not believe this was a good sample for comparative work as it was very wet.

R. C. Wiley: The denatured alcohol which was obtained by us for the potash work left a weighable residue upon evaporation and was therefore unsuitable for

[1] Mining and Engineering World, 1912, **36**: 605–606.

Coöperative results on potash.
(Percentage.)

ANALYST	SAMPLE 1: COMMERCIAL MURIATE OF POTASH — Official method	SAMPLE 1: COMMERCIAL MURIATE OF POTASH — Perchlorate method	SAMPLE 2: KAINIT — Official method	SAMPLE 2: KAINIT — Perchlorate method	SAMPLE 3: MIXTURE OF KAINIT AND ACID PHOSPHATE — Official method	SAMPLE 3: MIXTURE OF KAINIT AND ACID PHOSPHATE — Modified official method (hydrochloric acid omitted)	SAMPLE 3: MIXTURE OF KAINIT AND ACID PHOSPHATE — Official method, using denatured alcohol	SAMPLE 3: MIXTURE OF KAINIT AND ACID PHOSPHATE — Perchlorate method
T. D. Jarrell, College Park, Md.	51.33	51.75	12.57	12.63	6.07	5.94	[1]6.05	6.33
	51.95	51.38	12.50	12.45	5.95	5.93	[1]6.02	6.19
	51.80	51.55	12.43	12.35	6.01	5.99	[1]6.16	5.90
	51.68	52.15	12.62	12.48	5.98	5.90	[1]6.18	5.89
	51.25	52.10	12.66	12.69	5.95	5.93	[2]6.05	5.87
	51.80	......	12.58	12.39	6.07	5.92	[2]6.03	6.28
	51.80	......	......	12.42	6.03	5.96	[2]6.05	6.28
	51.54	......	......	......	5.94	6.01	[2]6.02	5.94
	......	......	......	......	6.06	......	[3]6.02	......
	......	......	......	......	5.95	......	[3]6.08	......
	......	......	......	......	6.02	......	[3]6.08	......
	......	......	......	......	5.94	......	[3]6.08	......
	......	......	......	......	5.93	......	......	......
Average	51.64	51.79	12.56	12.49	5.99	5.95	6.07	6.09
J. T. Foy, Clemson College, S. C.	......	......	......	......	5.97	6.06	[3]6.00	......
	......	......	......	......	6.12	5.89	[3]6.12	......
	......	......	......	......	6.02	6.08	[3]5.80	......
	......	......	......	......	6.10	6.08	[3]6.08	......
	......	......	......	......	6.03	5.96	[3]6.32	......
	......	......	......	......	6.01	5.84	[3]6.02	......
	......	......	......	......	5.93	5.88	[3]6.07	......
	......	......	......	......	5.93	6.03	[3]5.90	......
	......	......	......	......	5.81	5.92	[3]5.95	......
	......	......	......	......	5.98	5.76	[3]6.08	......
Average	......	......	......	......	5.99	5.94	6.04	......
A. Papineau Couture, Ottawa, Canada.	51.73	53.56	12.61	12.91	6.03	6.08	......	6.88
	51.82	53.41	12.60	13.02	6.13	6.04	......	6.93
	51.82	53.60	12.61	12.97	6.11	......	......	6.94
Average	51.79	53.52	12.61	12.97	6.09	6.06	......	6.92
E. E. Vanatta, Columbia, Mo.	49.98	49.94	12.06	12.50	6.06	5.82	......	5.71
	50.12	50.24	11.98	12.81	6.02	5.75	......	5.64
Average	[4]50.05	[4]50.12	12.02	12.66	6.04	[4]5.79	......	5.68
I. D. Sessums, Agricultural College, Miss.	51.96	52.23	12.02	13.30	6.18	5.87	......	8.09
	......	52.34	12.00	14.59	6.16	5.88	......	7.64
	......	......	......	14.30	......	......	......	7.62
	......	......	......	14.16	......	......	......	......
	......	......	......	13.68	......	......	......	......
	......	......	......	14.00	......	......	......	......
Average[5]	51.96	52.29	12.01	14.01	6.17	5.88	......	7.78

Coöperative results on potash.—Concluded.

(Percentage.)

ANALYST	SAMPLE 1: COMMERCIAL MURIATE OF POTASH		SAMPLE 2: KAINIT		SAMPLE 3: MIXTURE OF KAINIT AND ACID PHOSPHATE			
	Official method	Perchlorate method	Official method	Perchlorate method	Official method	Modified official method (hydrochloric acid omitted)	Official method, using denatured alcohol	Perchlorate method
J. J. Taylor, Atlanta, Ga.	52.30	52.08	12.50	12.10	6.17	6.29	......	6.19
	52.15	52.22	12.61	12.17	6.22	6.27	......	......
	52.30	......	......	......	6.26	6.17	......	......
Average[5]	52.25	52.15	12.55	12.14	6.22	6.24	......	6.19
O. B. Winter, East Lansing, Mich.	51.00	52.32	12.30	12.40	6.26	6.34	[2]6.14	6.16
	51.24	52.36	12.30	12.35	6.22	6.20	[2]6.16	6.12
	51.28	53.08	12.32	......	6.34	......	......	......
	51.28	......	......	......	......	......	......	......
Average	51.20	52.59	12.31	12.38	6.27	6.27	6.15	6.14
R. C. Wiley, Manhattan, Kans.	51.76	51.68	11.86	11.50	6.50	6.32	......	6.28
	52.20	51.35	12.22	11.76	6.24	6.28	......	6.48
	52.28	50.78	12.24	11.56	6.36	6.38	......	......
	51.44	50.92	12.56	12.65	6.32	......	......	......
	51.24	50.94	[6]11.54	12.48	......	......	......	......
	51.16	50.72	12.40	......	......	......	......	......
	......	52.02	12.02	......	......	......	......	......
	......	52.64	12.22	......	......	......	......	......
	......	......	12.52	......	......	......	......	......
Average	51.68	51.38	12.26	11.99	6.34	6.33	......	6.38
R. E. Ingham, Virginia-Carolina Chemical Co., Richmond, Va.	51.92	51.51	12.52	12.29	6.06	6.04	......	......
	52.00	51.89	12.56	12.36	......	......	......	......
Average	51.96	51.70	12.54	12.33	6.06	6.04	......	......
A. L. Gibson, Guelph, Canada.	50.41	48.04	11.89	10.03	5.26	......	......	4.96
	50.31	47.86	11.94	10.08	5.26	......	......	4.94
Average	[4]50.36	[4]47.95	11.92	[4]10.06	[4]5.26	......	......	[4]4.95
W. A. Davis, Rothamsted Experiment Station, England.	52.80	53.06	12.39	12.64	......	......	......	6.30
	......	52.92	......	12.70	......	......	......	6.40
Average	52.80	52.99	12.39	12.67	......	......	......	6.35
General Average	51.85	52.33	12.33	12.50	6.11	6.10	6.09	6.26

[1] 500 cc. of 95 per cent ethyl alcohol, 50 cc. of methyl alcohol, 2.50 cc. of benzene, 95 cc. of water.
[2] 400 cc. of 80 per cent ethyl alcohol, 100 cc. of methyl alcohol.
[3] 90 cc. of 80 per cent ethyl alcohol, 10 cc. of methyl alcohol, 1.50 cc. of gasoline, gas machine, 85° Baumé.
[4] Omitted from general average.
[5] Received too late to be included in general average.
[6] Omitted from average.

potash work. It is said to have been denatured with benzene. A weight of 2.9244 grams of potassium chloroplatinate was placed in four Gooch crucibles and washed with 80 per cent ethyl alcohol. The amount dissolved by 200 cc. of the alcohol was 1.40 mg. A second trial gave the same result. In my opinion, the perchlorate method is a little cheaper and a little quicker than the official method but I do not consider the difference as very great. It has been my experience that the results obtained by the perchlorate method are apt to be somewhat lower until one has had some experience in its manipulation. I found that with a little experience the results obtained by the perchlorate method were as accurate as those obtained by the official method.

R. N. Brackett: From a recent article published in the Journal of the American Chemical Society on the determination ot potash in soils by the perchlorate method, it appears that perchloric acid is now, or was before the present European war, an article of commerce. This fact seems to remove the chief difficulties in the use of this method. It appears to me that the work done, both in this country and in Europe has shown that the perchlorate method is practical and accurate and, of course, cheaper than the platinum chlorid method. With regard to the use of hydrochloric acid in the present official method of determing the potash in fertilizer, I may say that we have found that the addition of hydrochloric acid makes practically no difference in the final results, except in the case of acid phosphates with potash, with which the addition of the hydrochloric acid gives, I think, consistently higher results than without the addition of hydrochloric acid. I have thought that possibly it would be better if we continue to use hydrochloric acid that after the addition of the acid and boiling, ammonium oxalate be added to the acid solution and finally that ammonia be added sufficiently to make the solution slightly alkaline. This procedure ought, it seems to me, to prevent almost entirely, if not entirely, the precipitation of any phosphate of lime or of iron which is believed to retain potash.

F. B. Carpenter: We did not work the mixed fertilizer by the perchlorate method because we do not think it practical as compared with the platinum method.

A. L. Gibson: The weight of precipitate obtained from 0.25 gram of muriate of potash is very heavy. When it is known that a pure highly-concentrated potash salt, such as this, is being analyzed, it would seem better to reduce the quantity for analysis to 0.125 gram. The difficulties of thorough washing and careful manipulation of such a heavy precipitate would seem to increase the possibilities of error. The denatured alcohol used contained 95 per cent alcohol, of which about 10 per cent was methyl alcohol and 85 per cent ethyl alcohol. For washing potash precipitates, it was diluted with water so as to contain 80 per cent alcohol. For this experiment, a sample of complete commercial fertilizer sent to this laboratory for analysis was used. By washing the precipitate with denatured alcohol, made up as above, 12.33 per cent of potash was found, while with 80 per cent ethyl alcohol 12.28 per cent of potash was found. These experiments were made in duplicate, the results being practically the same showing very little difference between the use of 80 per cent denatured and 80 per cent ethyl alcohol.

W. A. Davis: The instructions given for the perchlorate method are likely to lead to some diversity of results and to some error, for the following reasons:

(1) When alcohol is first added to the sirup obtained after the evaporation with perchloric acid, the alcohol should not be alcohol already saturated with potassium perchlorate but 95 per cent to 96 per cent of alcohol alone. If alcohol saturated with the perchlorate is used at this stage, the perchloric acid present precipitates a trace of potassium perchlorate (due to the latter being less soluble in presence of perchloric acid) and the results are made slightly high in consequence.

(2) Instead of using 20 cc. of a mixture of alcohol and ether for the final washing, it is far more accurate to use for this washing only 95 per cent alcohol which has been previously saturated with potassium perchlorate at the temperature of working. The use of saturated alcohol for the whole washing does not add more than 0.0001 gram to the weight due to the presence of a trace of potassium perchlorate in the alcohol finally remaining in the asbestos, whereas the use of 20 cc. of a mixture of alcohol and ether causes the results to be too low by 3 or 4 mg., because of the relatively high solubility of potassium perchlorate in alcohol in the absence of perchloric acid (0.0070 to 0.0085 gram in 50 cc. of 95 per cent alcohol; see Davis, J. Agric. Sci., 1912, **5**: 65).

(3) The method of washing proposed in the instructions is unsatisfactory, the precipitate being always insufficiently washed when these instructions are followed precisely. This is shown by the fact that when the precipitate of potassium perchlorate obtained under the association instructions is again washed (after weighing) with alcohol saturated with potassium perchlorate, until the weight is constant, (using successive quantities of 50 cc. at a time for this purpose) a loss of weight of several milligrams is observed. This is particularly marked in the case of Sample 2 when the additional washing to constant weight lowered the result from 12.64 to 12.20 per cent of potash in one instance and from 12.70 to 12.42 per cent of potash in another.

I found 52.77 and 52.75 per cent of potash for Sample 1 and 12.39 and 12.43 per cent of potash for Sample 2 by my own method of washing. They are probably the correct results for the samples submitted. The method adopted was as follows:

After evaporating to a sirup (until heavy fumes of perchloric acid are evolved), cool and add 10 to 15 cc. of 95 to 96 per cent alcohol not previously saturated with perchlorate; break up the precipitate with a glass rod and stir well with the alcohol. Allow to stand for at least one-half hour before filtering and then decant the alcohol through the Gooch, thoroughly draining before adding the rest of the quantity of washing alcohol. For this second washing and all subsequent washings, 95 per cent alcohol saturated with potassium perchlorate at the temperature of working should be employed (see Davis, J. Agric. Sci., 1912, **5**: 65); at least 100 cc. of such alcohol should be used to insure that the washing is complete. I find it best in practice to wash one of the duplicate experiments with 100 cc. of this alcohol and the other with 150 cc. If there is any difference (more than 1 mg.) in the result, wash both duplicates with an extra 50 cc. of the alcohol saturated with potassium perchlorate. If the additional washing causes a loss of more than 0.0005 gram, the washing should again be repeated with another 50 cc. This, however, is seldom necessary, but only in this way is it possible to insure that the precipitate is thoroughly washed. In nearly all cases, the first 100 cc. of washing is sufficient and duplicates generally agree to 0.0005 gram, but in some cases especially when barium is present in large excess, the additional washing is necessary. The use of alcohol saturated with potassium perchlorate enables the washing to be carried out until the weight is quite constant, even when large volumes of the washing liquid (200 to 300 cc.) are necessary.

In showing the degree of accuracy of this method, I give a few results obtained by different operators in the ordinary routine work in this laboratory:

	Worker A.	*Worker B.*
Soil 1..........	0.1210 per cent of potash	0.1190 per cent of potash
Soil 2..........	0.0326 per cent of potash	0.0321 per cent of potash
Soil 3..........	0.3400 per cent of potash	0.3360 per cent of potash
Mixed fertilizer	7.4700 per cent of potash	7.4300 per cent of potash

Simplified process for estimating potash in mixed fertilizers.—Instead of adopting the successive treatment with sulphuric acid and barium chlorid as outlined in the instructions for Sample 3, it is far simpler and more rapid to use the following process: To a 50 cc. aliquot taken from flask after treatment with ammonium hydroxid and ammonium oxalate, add a slight excess of baryta (20 cc. of a 3 per cent solution of crystallized barium hydroxid) and without filtering evaporate to dryness in a porcelain dish, ignite for 15 minutes and extract thoroughly with boiling water, breaking up the precipitate with a glass rod in so doing. Filter and repeat the extraction with hot water until 100 to 150 cc. of the solution are obtained. Then add 5 cc. of perchloric acid and evaporate to a sirup in a glass dish, add another 5 cc. of perchloric acid and again evaporate until heavy fumes are evolved. Cool, add 10 to 15 cc. of 95 per cent alcohol and collect the potassium perchlorate as described.

This simple process eliminates sulphates, magnesium salts, ammonia, and organic matter in one operation. I received 6.30 per cent of potash for Sample 3 by the process outlined which shows that results are obtained that are identical with those given by the more troublesome process outlined in the instructions. This method is directly applicable to plant ashes and materials of this sort.

Use of glass dishes.—I always use glass dishes for evaporating the solutions containing perchloric acid and not a platinum dish. By using the glass dish it is possible to make sure that every trace of the crystalline potassium perchlorate is washed out of the dish into the Gooch crucible; this is not the case with platinum dishes. The crystalline precipitate often adheres firmly to the dish and when this happens it can easily be seen in a glass dish but is not visible in a platinum dish. Many special experiments have shown that not the least trace of potash is dissolved from the glass dish by the perchloric acid during the evaporation.

Use of denatured alcohol.—Experiments carried out some years back of which I have no longer the record, convinced me that the alcohol denatured with methyl alcohol or wood spirit can be safely used in all analyses by the perchlorate process, provided the alcohol does not contain much more than 5 per cent of water. We always use 95 per cent (duty free) grain spirit, which has not been denatured. With the platinum chlorid method, the use of denatured alcohol may give considerable error owing to the reduction of the platinic chlorid to metallic platinum by the impurities present in such alcohol. In such cases, when the potassium platinichlorid is dissolved in water after the analysis, a black film of metallic platinum is left in the asbestos of the Gooch. In carrying out the platinum process, I always wash with 80 per cent alcohol saturated with potassium platinichlorid. In this way, it is possible to wash to constant weight with large volumes of alcohol if necessary, without losing any of the potassium platinichlorid by dissolution.

Comparison of results by different methods.—Continued experience during the past three years has convinced me that the perchlorate method with the process of washing I have suggested is the most accurate method of estimating potash that yet exists. It is extremely simple especially in the case of soils and in the hands of different workers, the results agree in a surprisingly-close manner. On comparing the results for Samples 1 and 2, it is seen that the process outlined in the instructions give results 0.2 unit high, owing to insufficient washing; when washed to constant weight, the same material gives results 0.1 unit low owing to the dissolution of potassium perchlorate by the 20 cc. of alcohol ether more than outbalancing the extra weight caused by the use of alcohol saturated with potassium perchlorate at the first stage of the washing.

J. J. Taylor: My observations have led me to believe that the presence of hydrochloric acid is beneficial when complete fertilizers are boiled for any considerable time with water, giving almost without exception slightly higher results, but the difference is much less in the case of salts, such as muriates and kainits. For example, a sample was prepared of c. p. potassium chlorid and ground phosphate rock; only 90.08 per cent of the theoretical potash was obtained by the official method, while 98.73 per cent was obtained by the modified official. The perchlorate method proved very satisfactory with the salts (muriate and kainit) but difficult to duplicate closely with the sample of complete fertilizer. This may be due to unfamiliarity with the method as well as not having time to devote exclusively to the work. The result given on Sample 3 is the lowest one obtained, the other results (not tabulated) ranging from 0.4 to 1.6 per cent higher. In some cases these higher results were found to contain barium, but others did not. In the hands of a careful analyst, I believe this to be a good check on the Lindo-Gladding method.

E. E. Vanatta: A supply of denatured alcohol was made up according to Formula 1, Regulations No. 30, Revised: U. S. Internal Revenue. The results agree closely with those secured by using 80 per cent ethyl alcohol. We also purchased denatured alcohol from our local druggist. Results from the use of this alcohol were a little high, but were reduced to compare with other work after washing with 25 cc. more of same alcohol. Denatured alcohol, Formula 2, Regulations No. 30, Revised: U. S. Internal Revenue, gave very high results. The pyridin used precipitates the platinic chlorid and it becomes a measure ot amount of platinic chlorid addded rather than the amount of potash in the sample. Suspected denatured alcohol can be tested for the presence of pyridin by the addition of a small amount of platinic chlorid. Formation of precipitate shows alcohol unsuited for use in determination of potash. Contrary to expectations, results were low when the addition of 2 cc. of hydrochloric acid was omitted from potash solution.

Additional results on the loss in weight by washing a precipitate of potassium chloroplatinate with successive portions of 50 cc. of 80 per cent ethyl alcohol are given in the following table:

Loss by washing precipitate of potassium chloroplatinate with ethyl alcohol.

WEIGHT OF POTASSIUM CHLOROPLATINATE	LOSS, FIRST WASHING	LOSS, SECOND WASHING	LOSS, THIRD WASHING
gram	*gram*	*gram*	*gram*
1.1030	0.0015	0.0017	0.0019
1.1794	0.0025	0.0022	0.0015
0.5915	0.0018	0.0013	0.0013
0.6001	0.0017	0.0012	0.0012
0.3018	0.0015	0.0005	0.0007
0.3007	0.0010	0.0006	0.0002
0.2841	0.0010	0.0010	0.0004
0.2901	0.0015	0.0010	0.0005
Average loss......	0.0016	0.0012	0.0010

Average loss three washings, heavy precipitate, 0.0019 gram.
Average loss three washings, medium precipitate, 0.0015 gram.
Average loss three washings, light precipitate, 0.0009 gram.

A comparison of analysis of a solution containing known amount of potash using 80 per cent ethyl alcohol, denatured alcohol, and wood alcohol is shown in the following table:

One liter solution contained 2 grams of potassium sulphate, 2 grams of sodium sulphate, and 2 grams of magnesium sulphate, 25 cc. of solution drawn for each determination in triplicate; weight of potash in 25 cc. = 0.02703 gram (theory).

GRAMS OF POTASH WHEN WASHED WITH					
80 per cent ethyl alcohol	Denatured alcohol[1]	Denatured alcohol[2]	Denatured alcohol, bought on market	Denatured alcohol[3]	Wood alcohol
0.02700	0.02674	0.02708	0.02715	0.04037	0.02677
0.02673	0.02719	0.02684	0.02729	0.04154	....
0.02708	0.02706	0.02688	0.02731	0.03676	....
....	....	....	....	0.03676	....
Average 0.02694	0.02700	0.02693	0.02725	0.03932	0.02677

[1] 500 cc. of 95 per cent ethyl alcohol, 50 cc. of wood alcohol, 2.50 cc. of benzene, 47.50 cc. of water.

[2] 500 cc. of 95 per cent ethyl alcohol, 50 cc. of wood alcohol, 2.50 cc. of benzene, 95 cc. of water.

[3] 100 parts by volume of 95 per cent ethyl alcohol, 2 parts by volume of wood alcohol, $\frac{1}{2}$ part by volume of pyridin.

The following additional work was done on the official method and its modification by omitting the addition of hydrochloric acid on twenty-five samples of commercial fertilizer:

ANALYST	SAMPLE	OFFICIAL METHOD. POTASH	MODIFIED OFFICIAL METHOD. (HYDROCHLORIC ACID OMITTED). POTASH
J. T. Foy, Clemson College, S. C.	3082	4.83	4.87
	3086	3.43	3.40
	3087	3.62	3.68
	3363	5.11	4.99
	3365	5.15	5.00
	3362	3.95	4.04
	2650	2.82	2.82
	3559	3.89	3.94
	3557	3.19	3.28
T. D. Jarrell, College Park, Md.	30463	3.59	3.59
	30465	3.36	3.34
	30466	4.95	4.79
	30467	4.74	4.60
	30468	1.06	0.98
	30469	3.93	3.86
	30459	3.77	3.62
	30460	2.72	2.71
	30461	3.25	3.08
	30473	3.24	3.13
	30183	5.28	5.24
	30182	4.95	5.07
	30215	3.54	3.67
	30147	8.06	8.01
	30605	6.82	6.72
	30625	10.63	10.58
Average......................	....	4.40	4.36

DISCUSSION OF RESULTS.

PERCHLORATE METHOD.

The tabulated results by the perchlorate method show quite a variation. Some analysts seem to have no difficulty in getting results by this method which compare favorably with the official method, while other analysts do have trouble, largely due, no doubt, to inexperience with the method. There are unquestionably opportunities for errors to occur unless certain precautions are well understood and observed.

If a large excess of barium chlorid is added to the potash solution, it is necessary to add enough perchloric acid not only to combine with the potassium salt and other salts usually present in fertilizer materials, but also to combine with the excess of barium chlorid to change it to barium perchlorate. Therefore, there may be a tendency not to add sufficient perchloric acid to combine with all bases present. Should that occur, high results would be obtained because barium chlorid would be weighed with the potassium perchlorate. On the other hand, even if this precaution is observed, but the analyst washes the precipitate more than necessary, low results will be obtained, due to some of the precipitate being dissolved by the alcohol wash. A precipitate of potassium perchlorate weighing 0.4610 gram from c. p. potassium chlorid washed with successive portions of 50 cc. each of 95 per cent alcohol saturated at working temperature with potassium perchlorate and 20 cc. of an equal mixture of 95 per cent alcohol and ether gave a loss of about 0.0020 gram for each washing.

The perchlorate method in its present form for determining potash in mixed fertilizers is very unsatisfactory. It consumes too much time.

W. A. Davis of the Rothamsted Experimental Station, England, reports a simplified method which is outlined under Comments by Analysts. I have tried this method and secured very good results as compared with the official method. It has the advantage of being very much shorter.

It seems to me that with some modification, especially in the method of washing the potassium perchlorate, this method, in the hands of analysts familiar with its limitations, would give reasonably uniform and dependable results, and, therefore, deserves further study by the association.

USE OF DENATURED ALCOHOL FOR WASHING POTASSIUM-CHLOROPLATINATE.

Denatured alcohol used as a wash for potassium chloroplatinate gives results which agree favorably with 80 per cent ethyl alcohol in every case reported except when pyridin is used as one of the denaturing agents.

Vanatta reports that denatured alcohol containing pyridin cannot be used for potash work for the reason that pyridin precipitates the platinic chlorid, causing high results. The experience in our laboratory bears

out this statement. Denatured alcohol can be tested for the presence of pyridin by adding to it a few drops of platinic chlorid. If a precipitate forms, it cannot be used as a wash for potassium chloroplatinate when there is an excess of platinic chlorid present in the precipitate. The precipitate comes down very slowly.

I made up a supply of denatured alcohol according to the following formulas:

1..........	500 cc. of 95 per cent ethyl alcohol, 50 cc. of wood alcohol, 2.5 cc. of benzene, 95 cc. of water.	Formula 1. U. S. Internal Revenue Regulations No. 30—Revised. (August 22, 1911, p. 45).
2..........	400 cc. of 80 per cent ethyl alcohol, 100 cc. of methyl alcohol.	
3..........	360 cc. of 80 per cent ethyl alcohol, 40 cc. of methyl alcohol, 6 cc. of gasoline, gas machine, 85° Baumé.	

On Sample 3 by washing the potassium chloroplatinate with denatured alcohol, Formula 1, I obtained an average of 6.10 per cent of potash, with Formula 2, an average of 6.04 per cent of potash was obtained, with Formula 3, the average was 6.07 per cent of potash, and with 80 per cent ethyl alcohol, the average was 5.99 per cent of potash. The results by these three denatured alcohol formulas agree very closely with one another. They also agree very favorably with the 80 per cent ethyl alcohol, the denatured alcohol having the advantage of giving slightly higher results. The results show that ethyl alcohol denatured with methyl alcohol, benzene and methyl alcohol or gasoline and methyl alcohol, can be safely used for potash determinations. In all cases reported the analyst made up his own supply of denatured alcohol by adding known amounts of denaturing agents to 80 per cent ethyl alcohol.

MODIFIED OFFICIAL METHOD.

By comparing results by the official method with its modification by omitting the addition of 2 cc. of hydrochloric acid to the potash extract, it is seen that on Sample 3 an average of 6.11 per cent of potash was obtained by the official method and an average of 6.10 per cent of potash was obtained by the modified method, showing practically no difference between the two methods on this sample. On the twenty-five samples of commercial fertilizers reported by Mr. Foy of South Carolina and the associate referee, an average of 4.40 per cent of potash was obtained by the official method and an average of 4.36 per cent of potash was obtained by the modified method. Of these twenty-five samples, the official method is higher on sixteen samples, and the modified official method is higher on seven samples. The results are the same on two samples.

My experience with the modified method gives, in most instances, slightly lower results than the official method, while in other cases it gives practically the same results. In other words, it does not give uniformly lower results. These differences are well within the experimental error, and they may be due to accident rather than to the method. I believe it is well for the association to study next year the reason why the hydrochloric acid is added to the potash extract.

RECOMMENDATIONS.

It is recommended—

(1) That further study of the perchlorate method be made with special reference to the method for washing the potassium perchlorate precipitate.

(2) That coöperation be secured in testing the necessity for the addition of hydrochloric acid to the potash extract, with special reference to the reason why the hydrochloric acid is added.

(3) That denatured alcohol made up according to Formula 1 (Regulations No. 30—Revised, August 22, 1911, p. 45, U. S. Internal Revenue. 100 parts by volume of ethyl alcohol, not less than 180° proof, there shall be added 10 parts by volume of wood alcohol and one-half of one part by volume of benzene) with sufficient water added to make 80 per cent alcohol by volume, be made an alternate method for washing potassium chloroplatinate.

REPORT ON SOILS.

By J. W. Ames (Agricultural Experiment Station, Wooster, Ohio), *Referee.*

DETERMINATION OF CARBONATES AND ORGANIC CARBON.

The recommendations for work on soils to be undertaken during the year 1914, included a study of methods for determining organic carbon.

A correct figure for organic carbon in soils containing carbonates can not be obtained without applying the proper correction for carbon from inorganic sources. The official method for carbon dioxid in soils is somewhat indefinite. The method as given in Bulletin 107, Revised, states that it is to be determined as under analysis of inorganic plant constituents, by liberating carbon dioxid from soils with hydrochloric acid.

At the 1909 meeting of the association a report on carbonates in soils was made by the associate referee for that year. Since that time attention has been directed to the error introduced by the action of acid on soil organic matter with formation of carbon dioxid other than that from carbonates. Work by Marr (J. Agr. Sci., 1910, **3**: 156–160) shows that the action of dilute acid at atmospheric pressure is in some instances considerable. Results obtained in the laboratory of the referee lead to the same conclusion.

The importance of the question seemed to warrant further attention being given it; therefore, a comparison of two methods for the estimation of inorganic carbon dioxid was included in the work for this year.

Three soil samples were sent out with instructions outlining methods.

INSTRUCTIONS.

INORGANIC CARBON DIOXID.

Method A.—Use phosphoric acid (1 to 15), carbon dioxid free, for liberation of carbon dioxid; method proposed by McIntire and Willis in Tennessee Bulletin 100, Technical Series No. 1. (A copy of this bulletin together with photograph of shaking apparatus, supplied by Mr. McIntire, was sent out with instructions.)

Determine the carbon dioxid evolved either volumetrically or gravimetrically.

Method B.—Liberate carbon dioxid by heating soil with dilute hydrochloric acid under reduced pressure. (Procedure described by Marr, J. Agr. Sci., 1910, **3:** 155 and by Gaither, J. Ind. Eng. Chem., 1913, **5**, 138); for soils Nos. 1 and 3 use 20 grams; soil No. 2 use 5 grams.

Place soil in suitable flask of about 250 cc. capacity which will stand a vacuum of 70 cm. of mercury. Add 80 cc. of carbon-dioxid-free water, and after mixing thoroughly start suction pump. When air has been removed from apparatus and a vacuum of 65 to 75 cm. obtained, run into flask through separatory funnel 20 cc. of dilute hydrochloric acid (2 cc. of hydrochloric acid, specific gravity 1.19, to 18 cc. of water). Boil for 30 minutes at a temperature of 50°C. The bottom of the flask should be about three-quarters of an inch above gauze protecting it from free flame. If liquid in flask is drawn up into condenser tube, the flame should be lowered. Carbon dioxid evolved is absorbed in 4 per cent solution of sodium hydroxid made from sodium (25 cc. of 4 per cent sodium hydroxid solution and sufficient water to cover glass beads in absorbing tower). Relieve vacuum, wash out contents of absorbing tower with 150 cc. of carbon-dioxid-free water, using successive 25 cc. portions and titrate.

Titration.—For the assistance of those who have had no experience with the Brown and Escombe double titration method, the following details are given: Add 1 cc. of phenolphthalein to solution and run in normal hydrochloric acid until pink color begins to fade, then add twentieth-normal hydrochloric acid to complete disappearance of color. Take no account of normal or twentieth-normal hydrochloric acid used. When end point is reached, add two drops of methyl orange solution (1 gram per 1,000 cc.) and titrate with twentieth-normal hydrochloric acid until lemon color of alkaline methyl orange just darkens to slight orange color. Take reading of twentieth-normal hydrochloric acid and subtract correction obtained from blank determination run under same conditions. 1 cc. of twentieth-normal hydrochloric acid = 0.0022 gram of carbon dioxid. In this titration it will be necessary for each analyst to establish and adhere strictly to a constant end point for both indicators. It will be well for those not familiar with the titration to practice on a 4 per cent sodium hydroxid solution containing a small amount of sodium carbonate.

ORGANIC CARBON.

The instructions for determination of organic carbon requested that the total carbon dioxid found less that from carbonates be calculated to carbon and reported as organic carbon.

The results are reported as total carbon since the wide variation in the results by the two methods for inorganic carbon dioxid makes it impossible to obtain a correct figure for organic carbon from the determination of total carbon.

Transfer 3 grams of soil into a short-neck Kjeldahl nitrogen flask, or other suitable flask, and connect to apparatus. Run into flask 10 cc. of chromic acid solution containing 3.3 grams, then 50 cc. of concentrated sulphuric acid through separatory funnel. The mixture is boiled for 30 minutes during which time a moderate current of carbon-dioxid-free air is drawn through the boiling mixture. Carbon dioxid evolved is absorbed and titrated as directed under instructions for inorganic carbon dioxid.

RESULTS.

COMMENTS OF ANALYSTS.

E. Van Alstine: The results show a considerable amount of variation between the two methods suggested, and it is my belief that with many soils either method would give results much farther from the true amount of carbonate carbon present than would the method of boiling under atmospheric pressure with 1 to 1 hydrochloric acid. One variation difficult to explain is the fact that Samples 1 and 3 show a lower content of inorganic carbon by the Marr method than by the phosphoric acid method, while Sample 2 shows a higher content of inorganic carbon by the Marr method than by the phosphoric acid method. The results which we obtained by the Marr and McIntire methods indicate to me again that no analytical method can be relied upon, when it makes use of too many arbitrary conditions such as in this case the strength of acid and length of time to be boiled or shaken. With the Marr method there is the condition of pressure, which affects the boiling point.

Total carbon.

METHOD AND ANALYST	SOIL NO. 1	SOIL NO. 2	SOIL NO. 3
Referee method chromic acid combustion:	*per cent*	*per cent*	*per cent*
C. J. Schollenberger	0.8990	2.6200	1.0980
H. A. Noyes	0.9100	2.6600	0.9900
O. F. Jensen	0.9000	2.4510	1.0302
E. E. Vanatta	1.1729	2.6766	1.2815
W. H. Sachs	0.9130	2.4450	1.0410
S. D. Averitt	0.8650	2.3973	1.0533
L. G. Willis[1]	0.8073	2.4573	1.0664
Chromic acid combustion, gas passed over heated copper oxid: C. J. Schollenberger	0.9180	2.6341	1.1040
Combustion in furnace with copper oxid, carbon dioxid weighed C. J. Schollenberger	0.9434	2.6937	1.1285
Combustion in furnace; carbon dioxid weighed, corrected for carbon dioxid in ash: W. H. McIntire	1.0340	2.7030	1.2190
Wet combustion, 1 : 15 orthophosphoric acid, potassium dichromate; carbon dioxid weighed: W. H. McIntire	1.0390	2.7650	1.3280
Combustion with sodium peroxid; carbon dioxid gas measured: W. H. Sachs	0.8335	2.6577	1.097

[1] Used 3 grams of soil with 10 cc. of concentrated sulphuric acid containing chromic acid at rate of 3.3 grams per 50 cc.

Inorganic carbon dioxid.

ANALYST	SAMPLE 1		SAMPLE 2		SAMPLE 3	
	Method A (McIntire)	Method B (Marr)	Method A (McIntire)	Method B (Marr)	Method A (McIntire)	Method B (Marr)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. J. Schollenberger, Ohio	0.0110	0.0055	1.7380	2.3232	0.0286	0.0044
	0.0120	0.0055	1.7380	2.3276	0.0253	0.0033
	....	....	....	2.3144	....	0.0055
W. H. McIntire and L. G. Willis, Tennessee.	0.0180	0.0264	1.2680	2.2700	0.0210	0.0308
	0.0160	0.0188	0.3640	2.3000	0.0235	0.0297
	0.0155	0.0242	1.2540	2.2700	0.0245	0.0297
H. A. Noyes, Indiana	0.0066	0.0022	1.9000	2.0500	0.0044	0.0022
	0.0099	0.0022	0.8800	2.1200	0.0033	0.0022
	....	....	1.8300	....	....	....
	....	....	1.8400	....	....	....
	....	....	1.9500	....	....	....
O. F. Jensen, Michigan	0.012	0.0060	1.5900	2.1800	0.023	0.0300
	0.008	0.0050	1.6000	2.2400	0.018	0.0260
	0.008	0.0050	....	....	0.018	0.0200
	0.004	0.0070	....	....	0.019	....
	0.014	....	....	....	....	....
E. E. Vanatta, Missouri	0.0060	0.0633	1.408	2.2529	0.238	0.0558
	0.0060	0.0756	1.204	2.2529	0.087	0.0570
	....	....	....	....	....	0.0674
W. H. Sachs, Illinois	0.0098	0.0066	0.7278	2.0810	0.0176	0.0072
	0.0054	0.0039	0.7872	2.1120	0.0149	0.0066
	....	0.0033	0.7960	2.0460	....	....
	....	....	0.8004	2.1600	....	....
	....	....	0.7960	2.2260	....	....
	....	....	....	2.2570	....	....
	....	....	....	2.2480	....	....
S. D. Averitt, Kentucky	0.0070	0.0220	0.9880	2.2572	0.0070	0.0165
	0.0040	0.0143	1.0280	2.2310	0.0060	0.0176
	0.0053	....	1.0360	....	....	....

Other results for inorganic carbon dioxid reported by collaborators

McIntire-Willis procedure, shaking $2\frac{1}{2}$ hours. C. J. Schollenberger	....	....	2.2484	....	0.0374	....
1 : 15 hydrochloric acid constant agitation and 30 minutes aspiration C. J. Schollenberger	....	....	2.2350	....	....	....
Using 1 : 1 hydrochloric and boiling at 100° C. W. H. Sachs	0.0114	....	2.3536	....	0.0325	....
Boiling 1 minute with 1 : 15 phosphoric acid and aspirating 30 minutes. W. H. McIntire	....	....	2.2800	....	....	....
Using 1 : 15 hydrochloric acid and 4″ vacuum at room temperature for 30 minutes W. H. McIntire	....	....	2.2900	....	....	....

I am very much interested in these methods and in any other that may prove to get more accurately at the amount of inorganic carbon in all soils, realizing from our work here that the method of boiling with hydrochloric acid at 100°C. in common use at the present time gives results too high, probably in every case, when organic matter is present.

C. J. Schollenberger: Method A as described by McIntire and Willis in Tennessee Bulletin 100, does not appear to be satisfactory. The principal objections are slow evolution of carbon dioxid, and its retention in solution. From experiments made, both with soils and natural carbonates, it appears that the error due to slow evolution of carbon dioxid is in some cases considerable. As heating is not specified in the method, vigorous shaking and greater length of time is required. From results obtained with Sample 2, it appears that 2½ hours aspiration with continuous shaking at rate of 150 oscillations (2″) per minute, are required to extract all the carbon dioxid from this sample. This is shown by the following results:

Percentages of carbon dioxid evolved in various lengths of time from soil No. 2. 5 grams of soil; 65 cc. of 1 to 15 phosphoric acid, shaking and aspiration uniform.

EXPERIMENT NO.	CARBON DIOXID OBTAINED					
	In ½ hour (standard)	At end of 1 hour	At end of 1½ hours	At end of 2 hours	At end of 2½ hours	At end of 3 hours
1	1.535	....	....	....	....	....
2	1.549	[1]0.616	....	....	....	....
3	....	....	2.095	[1]0.066	[1]0.013	[1]0.00
4	....	....	....	....	2.262	[1]0.00
5	....	....	....	....	2.250	....

[1] The alkali was withdrawn from the absorption tower at the end of the period just preceding, titrated and replaced with fresh alkali, and the percentage given is the carbon dioxid found in this last portion of alkali. All precautions and blanks applied as usual.

The apparent action of orthophosphoric acid, upon soil organic matter is much greater than has been stated. Moreover, with some samples it is greater than with others, necessitating a separate blank for each.

Percentages of carbon dioxid liberated by 1 to 15 phosphoric acid from 3 samples, previously extracted by fifth-normal hydrochloric acid.

SAMPLE 1 (20 grams)	SAMPLE 2 (5 grams)	SAMPLE 3 (20 grams)
0.0011	0.0088	0.0220

On account of the necessity for continuous shaking of parts of the apparatus, the use of long lengths of rubber tubing becomes unavoidable. Rubber is said to absorb carbon dioxid selectively, and furthermore, its use increases the likelihood of leaks.

H. A. Noyes: I am more impressed with the McIntire than with the Marr method for soil carbonates as I believe it will give satisfactory results on all types of soil, peats included. Low results obtained in the use of the McIntire method are due to not bubbling air through to complete exhaustion of carbon dioxid. I believe that the determination should be run in the apparatus as described in *Journal of Industrial and Engineering Chemistry*, 1914, volume 6. Allow air to bubble slowly through

flask D throughout the determination. By opening the pump more every few minutes, the pressure in apparatus is gradually reduced, the carbon dioxid being expelled by the air, and the contents of the flask agitated throughout the whole half-hour of the air current.

E. E. Vanatta: The chemist doing this work failed to get satisfactory results by Method A. This may be due to the fact that the method was new to him. The results secured by Method B and for total carbonates were fairly concordant and would perhaps give closer agreement after the chemist has had more experience with the method. There is no great difference in the time required by the two methods.

O. F. Jensen: While the double titration method for determining carbon dioxid may give good results after some experience is gained in reading the end points properly, I believe that a gravimetric method is much more accurate, especially where large amounts of carbon dioxid are to be determined. Gomberg potash bulbs were used very successfully instead of the soda-lime tubes in the McIntire method.

S. D. Averitt: I am convinced from the present work and from a great deal of previous work along this line, that if the solution is heated, organic matter will be attacked, and that the resulting figure for inorganic carbon dioxid will be too high. Method A is easier of manipulation than method B and I believe will give nearer the correct values for inorganic carbon dioxid.

W. H. McIntire: We are very much interested in the soil marked No. 2, the organic matter content of which does not seem to be affected by boiling with acid, and we wonder if it is synthetic. We have been running soil under field treatment which contains many times the amount of carbon dioxid contained in soil No. 2, as a result of the application of nearly 400,000 pounds of an ordinary grade of limestone to 2,000,000 pounds of soil, and we have had no difficulty in securing all the carbon dioxid therefrom. In soil No. 2, however, there seems to be an extended action of phosphoric acid. Our method checks both the Marr and official method when using 1 to 15 hydrochloric acid.

In working up the McIntire-Willis procedure, it was intended to run the method gravimetrically using phosphoric acid and thus simplify the apparatus by the elimination of sulphate tubes. We have now adopted a titration procedure and the hydrochloric acid is not objectionable since the action of 1 to 15 hydrochloric acid at room temperature is hardly estimable from a 5 gram charge used. I might state, however, that we have made a thorough test of the Folin tube and the bead tower apparatus and find that the Folin apparatus will absorb carbon dioxid from ordinary soils but that it will not fix all carbon dioxid in exceedingly heavy charges unless the aspiration is so slow as to make its use unfeasible.

RECOMMENDATIONS.

It is recommended—

(1) That a further test of methods for the determination of soil carbonates be made, comparing the Marr procedure with methods which involve the use of dilute hydrochloric acid (1 : 15) and constant aspiration of air with and without heating.

(2) That the wet combustion method with mixture of chromic and sulphuric acids for estimation of organic carbon be further compared with combustion of soil in furnace.

(3) That at the suggestion of Mr. Shedd of Kentucky, a study be made by the association of a method for lime requirement of soils by H. B.

Hutchinson and K. McLennan, published in Chemical News, August 7, 1914. (This method makes use of a solution of calcium bicarbonate for satisfying the lime requirement of soils.)

A NEW METHOD FOR THE DETERMINATION OF LIME REQUIREMENTS IN SOILS.

By W. H. McIntire (Agricultural Experiment Station, Knoxville, Tenn.).

The results of recent investigations seem to justify the conclusion that fallacies enter into the various methods advanced for the determination of lime requirements of soils, where the analytical procedures involve the use of substances other than hydrate or carbonate of lime.

For instance, there is a marked difference between a soil's assimilation of magnesium, through decomposition of carbonate with the resultant formation of magnesium silicate, and the amount of calcium carbonate decomposed by the silicic acid reaction. Yet these two carbonates have long been considered as closely parallel in their activities toward acid-acting soil components.

The investigations conducted during the last three years at the Tennessee Agricultural Experiment Station have resulted in the evolution of a method which combines both speed and accuracy, if the latter be measured by securing a maximum activity and closely-concordant results.

The studies preliminary to the advancement of the method have led to the conclusion that the maximum reaction to be obtained between lime and soils, under laboratory conditions involving comparatively brief periods of contract, are to be secured by the procedure. The thought prompting the work was to effect a dissemination of dissolved carbonate of lime throughout the soil mass and to effect precipitation of the carbonate under conditions as nearly corresponding to those of the field as possible.

Only the essentials of the method are given at this time, but the details will be published in full later, together with certain of the results secured in preliminary study.

A stock solution of carbonate of lime in solution is obtained by passing a current of carbon dioxid through about 10 grams of "fluffy" precipitated calcium carbonate suspended in 5 liters of distilled water. The purified carbon dioxid gas may pass through the mixture of carbonate and distilled water overnight. The excess of carbonate is removed by gravity filtration. The clear solution of dissolved calcium carbonate is received, in about one-tenth of its volume of carbonated distilled water. This filtered and diluted solution is kept cool and under pressure. Pipette 100 cc. of the carbonate solution into a 150 cc porcelain evaporating dish and add 10 grams of $\frac{1}{2}$-mm. or 100-mesh soil. Evaporate to a thin paste, the mixture being stirred after the precipitation of the calcium carbonate

from solution and again when reaching volumes of about 75 and 50 cc. The paste is then used to effect scouring of the sides of the evaporating dish by means of a rubber tipped glass rod. The soil is then washed into a 300 cc. Erlenmeyer flask by means of carbon-dioxid-free distilled water to a volume of about 60 cc. A series of flasks are then connected with a shaking device (Tenn. Agric. Exper. Sta. Bul. 107), 5 cc. of 85 per cent phosphoric acid are added and the liberated residual carbon dioxid determined by passage of the gas through 25 cc. of 4 per cent sodium hydroxid in a Camp absorption tower, the air passing into the system, being of course, first purified of carbon dioxid. Carbon-dioxid-free distilled water is used to increase the volume of 25 cc. sodium hydroxid to an amount sufficient to cover the beads before the passage of carbon dioxid through the absorbent solution. A vacuum of 4 inches is maintained in the apparatus during the 30 minutes agitation and aspiration.

The amount of calcium carbonate in 100 cc. of the carbonate solution is determined by boiling off the excess of dissolved gas and decomposing the precipitated carbonate by the above procedure. The difference between the added and the residual calcium carbonate in the soil is then determined, correction being made for the carbon dioxid in the atmosphere of apparatus and the carbonate in the sodium hydroxid solution.

THE INTERPRETATION OF SOIL ANALYSES.

By G. S. Fraps (Agricultural Experiment Station, College Station, Tex.).

The chemical analysis of soils is made by three widely-differing methods. The first consists of estimating the total quantity of plant food and other constituents of the soil; the second in determining the plant food soluble in strong hot hydrochloric acid; the third in determining the phosphoric acid, the potash, and the lime soluble in weak solvents. Fifth-normal nitric acid is often used for this purpose although other solvents are used. The estimation of the total plant food by the first method includes not only that which is easily taken up by the plant, but also that contained in difficultly-soluble silicates, such as feldspar. The quantity of total phosphoric acid is usually very nearly the same as that soluble in strong hydrochloric acid. The total potash is very different from that soluble in strong hydrochloric acid, and includes the potash in highly-refractory silicates. The total nitrogen is estimated in all three methods, as we have as yet no method for distinguishing accurately between the different forms of nitrogen in the soil.

The estimation of the total plant food is considered by some chemists to be of great advantage, but I have not yet found in chemical literature any careful scientific study of the relation between the total plant food and soil deficiencies, which brings out clearly the relation of these two.

There have been expressions of opinions, but these opinions have not been accompanied by a marshalled array of facts, susceptible of verification and study.

The potash and phosphoric acid soluble in strong hot hydrochloric acid have been estimated in a large number of soil analyses. There are great differences in the standards used by various chemists in the interpretation of the results. The interpretation used in this country is usually based upon the observations of Hilgard, aided probably by other observations of the chemist interpreting the results, which, of course, may be different in different localities. Full data upon which these interpretations have been made have not been clearly and definitely published so far as I can ascertain. It appears to be certain, however, that progress has been made in the interpretation of results of such an analysis, and that, though the analyses and interpretations show differences of opinion, they give fairly good information as to the wearing qualities of the soils. Different interpretations may also be necessary under different climatic conditions. The standards used by the author, which are subject to change, are published in Bulletin 161 of the Texas Agricultural Experiment Station.

Work done at the Texas station has brought out the average relation between the results of pot experiments, the total nitrogen of the soil, and the phosphoric acid and potash soluble in fifth-normal nitric acid.

In Bulletin 151 of the Texas station is shown that the deficiency of the soil in nitrogen in pot experiments is related to the total nitrogen of the soil. This is based on 332 experiments. In Bulletin 126 of the same station is brought out the fact that the deficiency of the soil as shown in pot experiments is related to the active phosphoric acid of the soil; in Bulletin 145, that the deficiency in potash in pot experiments is related to the active potash of the soil. These results are averages, and bring out rather clearly and definitely the fact that there is an average relation between the total nitrogen, the active phosphoric acid, the active potash and the average deficiencies of the soils for these plant foods in pot experiments.

It is well known that there are wide deviations from the average in individual cases. It is necessary to study these individual cases and ascertain the causes of such variation. It is also known very well that there are soils which, though well supplied with plant food, do not give average crops; that is, the deficiency is due to something else than the deficiency of plant food. Experience has also shown, that though the pot experiments do not always confirm the chemical analyses, yet the pot experiments are themselves open to irregularities, and further experiments on the same soil reduces the number of discrepancies between the analyses and pot tests.

Beyond a doubt, there are differences in the plant food supplied to plants by various types of soils depending on other factors than the active

phosphoric acid, the active potash and the total nitrogen. The quantity of active phosphoric acid may be greater than the analysis shows, if the soil has a high fixing power for phosphoric acid. The total phosphoric acid may be more easily taken up by plants from certain soils than from others. The total potash may lend more of its potash in some soils than others. The active potash of soils, however, is highly available to plants. In some soils, more than others, a larger percentage of the nitrogen is in forms easily acted upon by bacteria and converted into nitrogenous compounds that can be taken up by the plant. These differences leave us abundant room for further study, but, in the meantime, the method of interpretation here described may be considered as a forward step.

The following table shows the standards of interpretation now used by us:

NITROGEN		POTASH		PHOSPHORIC ACID	
Total nitrogen	Corn equivalent	Active potash	Corn equivalent	Active potash	Corn equivalent
per cent	*bushels*	*parts per million*	*bushels*	*parts per million*	*bushels*
0.000–0.02	8	0– 50	29	0– 10	6
0.021–0.04	13	51–100	37	10.1– 20	12
0.041–0.06	18	101–150	51	20.1– 30	18
0.061–0.08	23	151–200	80	30.1– 40	24
0.081–0.10	28	201–300	120	40.1– 60	30
0.101–0.12	33	301–400	157	60.1– 80	35
0.121–0.14	38	401–600	182	80.1–100	40
0.141–0.16	43	601–800	207	100.1–200	45
0.161–0.18	48			200.1–400	50

The results are interpreted upon the basis of corn, as it brings out more clearly the relative deficiencies of a soil. Other crops than corn might be used but most of our pot experiments were conducted with corn and deficiencies shown with corn are usually deficiencies shown with other crops. Suppose a soil contains 18 parts per million of active phosphoric acid, 120 parts per million of active potash, and 0.09 per cent total nitrogen. The average relative deficiency for corn would then be, 12 bushels for phosphoric acid, 51 for potash, and 28 for nitrogen. The soil is thus clearly most deficient in phosphoric acid and least deficient in potash.

The fact must be emphasized that the interpretation just given is relative not absolute. In a series of pot experiments, the soil might produce differently under local conditions of temperature, weather, and soil treatment; run under more favorable conditions, might well give higher figures throughout the table. Our own more favorable pot experiments would give higher results. Pot experiments with different plants or elsewhere would give somewhat different absolute results. The relative results would probably agree more closely. The table, then, does not show the bushels of corn per acre that the soil should produce, but its value lies in

showing the relative deficiencies of the soil by means of the chemical analysis. These relative deficiencies should, on an average, hold good. Undoubtedly, as previously pointed out, there are exceptions.

The application of the result of the analysis to field conditions, is a difficult matter. There must first be considered what the soil actually produces, and then what is the possible production under such conditions. If we can introduce other improvements to increase production possibilities, then we may raise our suggestions for plant food.

The plant food may not be the limiting factor in production; in fact, other factors are often of great significance. A soil supplying phosphoric acid sufficient for 20 bushels of corn, is not necessarily deficient in phosphoric acid; the limiting factors may be something else. It would be useless to supply phosphoric acid without improving the limiting conditions. The chemical analysis would then be said to have been at fault, but the fault would lie elsewhere. It would be useless to fertilize a field for 50 bushels of corn, when other factors limit its production to 30.

Hence, in applying our chemical analysis to field conditions, we must consider the possibility of other limiting conditions, and make our suggestions upon the basis of soil conditions and soil treatment as they exist in the locality in question.

This point is emphasized because soil analysis has been blamed, when the fault was really elsewhere. The method of analysis and interpretation given in this paper, has proved of great service in studying Texas soils and in making suggestions as to plant food and soil treatment to be used on them. By considering the local soil conditions, and the actual production, in connection with the analysis, gratifying results have been secured. The method has also proved very useful in selecting soils to be used for pot experiments to test the availability of phosphates, potash, or nitrogenous compounds. The possibility of the unfertilized soil to produce a crop of corn, can usually be determined by means of the analysis.

The method has also proved of great service in connection with further studies of the plant food of Texas soils. For this purpose, the soils are divided into groups according to their content of the plant food under investigation, and then these groups, under the same conditions, are subjected to further study. For example, a study of the production of nitric nitrogen in 322 Texas soils is now in process, and it has been found, among other things, that the production of nitrates, on an average, is related to the total nitrogen of the soil.

In conclusion, I will say that the estimation of the total nitrogen, the active phosphoric acid, the active potash and the acid consumed of the soil at present affords the best measure of the soil fertility and the best means of judging of its deficiencies. Considerable study is yet needed in order to ascertain the relation of the different types of soil to these analyses, and to ascertain the causes of the deviations from the average results.

REPORT ON NITROGENOUS COMPOUNDS OF SOILS.

By C. B. Lipman (Agricultural Experiment Station, Berkeley, Cal.), *Associate Referee.*

Owing to his late appointment following the resignation of Oswald Schreiner, the associate referee on nitrogenous materials in soils has been unable to inaugurate studies which could possibly yield results at this date. Moreover, it seems that the association has been giving much time to the study of methods in soil chemical work which are already well established and have been neglecting to study methods now in use which need much improvement. I beg, therefore, briefly to call your attention, in lieu of the usual report, to the present status of some methods employed in soil chemical work so that they may be discussed and steps be taken for next year's work.

METHODS FOR THE DETERMINATION OF AMMONIA IN SOILS.

There seems to be no necessity of having soil chemists investigate further the methods for ammonia determination in soils. In both ordinary soil chemical and soil bacteriological work, the present methods of distilling ammonia over from the water suspension of the soil with magnesium oxid added seems to satisfy the purposes very well. Those who desire to separate ammonium compounds from the closely-related organic compounds in soils may, of course, employ methods of the organic chemists such as those proposed by Jodidi and others who have worked on the organic nitrogenous constituents of soils.

So far as the Nessler method for determining ammonia is concerned the results are very satisfactory when small amounts are to be determined, but the method is rarely used in soil work. If it needs improvement, why should not that improvement be carried out by the water chemists who have far greater use for the method than the soil chemists?

METHODS FOR THE DETERMINATION OF NITRITES IN SOILS.

The present methods for nitrite determination in soils leave much to be desired. It is very difficult in using the sulphanilic acid and alpha naphthylamin method for the determination of nitrites to maintain constant color in the standard solution used for comparison, thus introducing, especially when small amounts are sought, a very considerable error. Then, too, soil solutions never have the same tint as the standard solution and comparison, therefore, is made additionally difficult.

Here again I would recommend that owing to the relative unimportance of the determination of nitrites in soils and the much greater importance

thereof in water analysis that methods for nitrite determination or for the determination of nitrous acid, be left for perfection to the water chemists or others who may be more directly interested.

METHODS FOR THE DETERMINATION OF NITRATES IN SOILS.

The phenoldisulphonic acid method or the colorimetric method for the determination of nitrates is now, after considerable modification, an excellent method for use in soils free from salts. Very careful and extensive tests thereof and changes in the manipulation which Professor Sharp and the present associate referee carried out some time ago and reported on in full, have made it easy to use the method and to obtain very good results therewith. It does not seem at the present time that very much improvement can be made on this method of determining nitrates in the soil solution. I would therefore recommend to you that the phenoldisulphonic acid method as thus modified be adopted as the official method for the determination of nitrates colorimetrically.

So far as the nitrate determination is concerned, in a soil extract containing salts, which have been shown to interfere seriously with the phenoldisulphonic acid method, the reduction method is decidedly the one which can be relied upon most for accurate results. Reduction with either iron or aluminum will give good results as shown by Professor Hill of the Virginia experiment station and Professor Burgess of the California experiment station respectively. I think that there is no question that the manipulation in the aluminum reduction method is very much the simpler of the two. The results obtained are as accurate as any that can be expected in chemical work or in analytical work, and I would therefore recommend that the aluminum reduction method as modified by Professor Burgess, be adopted as the official reduction method for nitrates in soils.

METHODS FOR THE DETERMINATION OF TOTAL NITROGEN.

It is in these methods more than in any other that it seems that the association should be carrying on some investigations. None of the methods now in vogue and used as official or unofficial, make sure of the exclusion of nitrates when all the nitrogen in soils minus the nitrates is sought. Likewise the methods for the inclusion of nitrates do not always show all the nitrates.

Thus in the first set of methods is included some of the nitrate nitrogen and in the second set of methods not all the nitrates. This should be taken up as a subject of investigation and methods established soon which will make possible the determination, readily, of all of the nitrogen in the soil exclusive of the nitrate nitrogen so that one may easily separate all other forms from the latter. It becomes very necessary to

have this separation very frequently in soil work and in fact it is essential to the success of some work. I would therefore recommend that the association investigate methods for the determination of the total nitrogen in soils (minus the nitrates) for the purpose of improving them.

The suggestions made are for the purpose of stimulating discussion of the subject and are not given in any spirit of criticism. If they will serve to help soil chemists attain more accurate methods for the determination of various nitrogenous materials in soils, and if they will do so quickly and definitely, I shall feel well repaid.

REPORT ON ALKALI SOILS.

By R. F. Hare (Agricultural Experiment Station, State College, N. Mex.), *Associate Referee.*[1]

Since this is the first year the association has undertaken a study of methods for the analysis of alkali soils, it was thought best not to attempt coöperative work for this year, but to devote the time at the disposal of the associate referee to a comparison of the methods now in common use, and to present a review of these to the association, with some criticisms, and suggestions as to the phases of the work that, in the opinion of the associate referee, should be studied for the coming year.

Before many experiments are undertaken on a comparison of methods for the analysis of alkali soils, it would seem advisable for those interested to agree upon the following points: (1) Proper method of sampling; (2) substances to be determined; (3) method of reporting results.

The associate referee would suggest that the association act on these points at the November meeting, and recommends that the associate referee for the coming year be instructed to ask coöperation in determining the following: (1) The best method for obtaining the soil solution; (2) A comparison of the common methods at present in use for "black alkali" determination.

In the following paper on some of the methods for the determination of alkali in soils the associate referee has attempted to outline briefly some of the methods now in use, and to offer some suggestions as to the points that in his opinion should be mutually agreed upon before the work on methods for obtaining the solution and determining the "black alkali" are undertaken.

The results for the determination of soluble solids, chlorids, and carbonates in three Arizona soils by methods in use in seven different laboratories are given in this paper. These were compiled from analyses made by Vinson and Catlin and published in the Arizona Agricultural Experiment Station Annual Report, Number 24, page 276. These figures are

[1] Read by B. B. Ross.

TABLE 1.

Comparison of results obtained for black alkali by three different methods.

SOIL NUMBER	NEW MEXICO METHOD[1]		CALIFORNIA METHOD, MODIFIED[2]		ARIZONA METHOD, MODIFIED[3]	RESULTS BY NEW MEXICO METHOD CALCULATED TO SODIUM CARBONATE	RESULTS BY CALIFORNIA METHOD CALCULATED TO SODIUM CARBONATE
	Sodium carbonate	Sodium acid carbonate	Sodium carbonate	Sodium acid carbonate	Sodium carbonate		
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	0.022	0.191	0.158	0.153	0.153	0.143	0.255
2	0.050	0.187	0.171	0.180	0.204	0.168	0.285
3	0.017	0.175	0.072	0.110	0.178	0.127	0.141
4	0.008	None	None	0.022	None	0.008	0.014
5	0.011	None	None	0.009	None	0.011	0.006
6	0.006	None	None	0.009	None	0.006	0.006
7	0.011	0.211	0.111	0.118	0.170	0.144	0.185
8	None	0.048	0.011	0.042	0.042	0.030	0.037
9	None	0.018	0.017	0.031	0.017	0.011	0.037
10	0.113	0.176	0.166	0.167	0.233	0.224	0.271
11	None	0.119	0.033	0.062	0.098	0.075	0.072
12	None	0.077	0.019	0.026	0.042	0.049	0.035
13	0.446	0.015	0.453	.....	0.382	0.455	0.453
14	None	0.050	0.037	0.048	0.051	0.032	0.067
15	0.204	0.193	0.337	0.289	0.372	0.326	0.519
16	0.050	0.172	0.160	0.160	0.203	0.159	0.261
17	None	0.026	0.030	0.033	None	0.016	0.051
18	0.017	0.151	0.100	0.063	0.170	0.112	0.140
19	0.017	0.129	0.111	0.063	0.140	0.098	0.151
20	0.003	0.116	0.069	0.105	0.119	0.076	0.135
21	None	None	0.044	None	None	None	0.044
22	0.006	0.138	0.110	0.101	0.110	0.093	0.174
23	None	None	None	None	0.017	None	None
24	0.260	0.205	0.350	0.319	0.390	0.389	0.551
25	0.032	0.178	0.276	0.231	0.195	0.144	0.422
26	0.005	0.065	0.064	0.071	0.092	0.046	0.109
27	None	0.120	0.064	0.059	0.092	0.076	0.101
28	0.482	0.083	0.482	0.403	0.492	0.534	0.736
29	0.196	0.204	0.307	0.286	0.297	0.325	0.487
30	None	0.171	0.106	0.126	0.110	0.108	0.185
31	0.016	0.218	0.159	0.164	0.187	0.154	0.162
32	0.056	0.222	0.180	0.172	0.246	0.196	0.289
33	0.201	0.223	0.329	0.294	0.424	0.342	0.514
34	0.536	0.365	0.562	0.479	0.806	0.765	0.864
35	None	0.212	0.127	0.172	0.161	0.134	0.235
36	0.037	0.080	0.095	0.092	0.119	0.087	0.153
37	0.111	0.069	0.159	0.151	0.195	0.155	0.254
38	0.011	0.014	0.019	0.040	0.034	0.020	0.044
39	0.037	0.120	0.118	0.024	0.102	0.113	0.133
40	0.016	0.112	0.088	0.004	0.085	0.087	0.091
41							
1st foot	0.311	0.209	....	....	0.508	0.443	....
2d foot	0.311	0.209	....	....	0.480	0.443	....
3d foot	0.286	0.201	....	....	0.449	0.413	....
4th foot	0.286	0.201	....	....	0.415	0.413	....

[1] Association method for irrigating waters.

[2] By this method the soil filtrate was evaporated gently, ignited, redissolved in freshly-boiled water, and titrated for sodium carbonate, sodium acid carbonate and potassium acid sulphate.

[3] Association method for "black alkali."

in themselves sufficient to convince one of the necessity for uniformity in our methods of alkali soil analyses.

During the year the associate referee has made alkali analyses of a number of New Mexico soils from a region in which "black alkali" is the dominant type. In these analyses 50 grams of soil were treated overnight with 500 cc. of water, and total solids, calcium, magnesium, sodium (by difference), sulphates, chlorids, carbonates, and bicarbonates were determined from the filtrate obtained by passing through a Chamberlain-Pasteur filter. These ions were reported as such, and also as salts, calculated by the methods of this association for irrigating waters, as given in Bureau of Chemistry Circular 52. The results for sodium carbonate and bicarbonate (black alkali) obtained by this method are given in Table 1, together with results obtained on the same soils by modifications of methods in use in the Arizona and California laboratories.

The Arizona method is the one given for alkali waters of this association. The only modification of their method was in the preparation of the soil solution, which was prepared in a similar manner for all three methods. In California the soil filtrate is evaporated to dryness, gently ignited, redissolved in freshly-boiled water, and titrated with standard acid. The method was modified in these analyses by using a different proportion of water to obtain the soil solution, and by titrating with standard potassium acid sulphate to distinguish between carbonates and bicarbonates. The results do not show a sufficiently close agreement by the three methods. As a rule, the California method gives high results.

The associate referee would recommend that the association method for alkali waters be provisionally adopted for alkali soils. By this method the carbonates and bicarbonates of sodium calculated from the ions are checked by the method for black alkali.

A REVIEW AND DISCUSSION OF SOME OF THE METHODS FOR THE DETERMINATION OF ALKALI IN SOILS.

By R. F. Hare (Agricultural Experiment Station, State College, N. Mex.).

INTRODUCTORY.

In those localities where a scant rainfall and insufficient drainage result in the accumulation of soluble salts in sufficient quantity to injure crops, or entirely prevent their germination and growth, a determination of the amount and character of these salts becomes even more essential than a study of the plant food content of the soil.

The Bureau of Soils of the United States Department of Agriculture, several of the western experiment stations, and some foreign countries

have made numerous analytical investigations on alkali soils; but, as Whitney pointed out several years ago, the procedures and methods of analysis employed have been almost as numerous. If all the various methods of analysis employed gave correct results, the lack of uniformity in collecting samples and of reporting results make comparative studies of investigation carried on in different localities practically worthless. But Vinson and Catlin[1] have shown that the methods of analysis used in seven different laboratories, when tried by them on three Arizona soils, gave far from concordant results. By some of these seven methods black alkali is indicated in the soil in excess of the usually accepted toxic limits of cultivated plants, while by other methods the same soil shows no black alkali at all, but a considerable quantity of gypsum, which is a corrective for this alkali.

The methods for the determination of black alkali (Na_2CO_3 and $NaHCO_3$) are the ones that seem to require the most attention at present.

COMPOSITION OF ALKALI TYPES.

All the types of alkali to be found in different localities are principally composed of the soluble salts of the four acid radicals, chlorids, sulphates, carbonates and bicarbonates, in combination with the three bases, calcium, magnesium and sodium. The small amounts of other radicals that may be found in most alkali soils or waters is perhaps negligible, so far as their toxic effect on plants is concerned. The determination of those radicals mentioned above is sufficient to enable one to judge of the character of the soluble salts that constitute the alkali, except perhaps in a few localities where nitrates seem to have accumulated in injurious quantities. In some cases where the alkali type is known, only a few of these radicals are determined in judging of the fitness of soils for certain crops.

COLLECTION OF SAMPLES.

The movement of alkali salts with the water in soil makes careful sampling necessary, and the results of different investigators can be of little value unless the samples are taken with some degree of uniformity.

Notes on methods of sampling, depth, locality, topography, vegetation, texture of soil and subsoil, position of water table, drainage conditions, rock formation and date of last irrigation or rain help in an interpretation of the analyses.

Not less than one pound of soil is usually collected from each foot to a depth of four to six feet, placed in air tight vessels, and a portion used for total moisture determination. In some cases it may be necessary to

[1] Ariz. Agr. Exper. Sta., 24th Ann. Rep.

sample deeper than six feet, while under certain circumstances less than this depth is sufficient. When the time of the investigator is limited, a composite of the different depths is sometimes made.

The soil should be air dried and passed through a 1 mm. sieve before proceeding with the analysis.

PREPARATION OF THE SOLUTION.

The alkali determination is made from the water solution of the soil, and the proportion of soil to water used by different investigators varies greatly. At the California Station 300 cc. of water are added to 150 grams of soil; while in Arizona the proportion is 1,000 cc. of water to 50 grams of soil. The fact that the different investigators use so many different proportions of soil to water makes any comparative study of at least some of the determinations of little value. In Table 1 is given a compilation of results by Vinson and Catlin on three Arizona soils by the methods in use in seven different laboratories.

TABLE 1.

Comparison of results obtained by different methods for sodium chlorid, total solids, and sodium carbonate in three Arizona soils by Vinson and Catlin.[1]

(Calculated to per cent air dry soil.)

LABORATORY	PROPORTION OF SOIL TO WATER	SODIUM CHLORID			TOTAL SOLIDS			ALKALINITY AS Na_2CO_3		
		Soil			Soil			Soil		
		1	2	3	1	2	3	1	2	3
California	100 to 200	0.112	0 004	0.283	0.531	0.046	3.008	0.230	0.023	0.017
Montana	100 to 500	0.109	0.004	0.288	0.551	0.070	3.715	0.257	0.048	0.013
Bureau of Soils	100 to 500	0.105	0.004	0 297	0.528	0.069	3.618	[2] 0.221	[3]	[4] ....
Texas	100 to 500	0.112	0.004	0.295	0.555	0.068	3.698	[5]	[6]	[7]
New Mexico	100 to 1000	0.107	0 004	0.304	0.584	0.094	3.429	0.283	[8]	[9]
Utah	100 to 1000	0.114	0.004	0.300	0.632	0.116	4.192	0.394	0.081	0.038 [10]
Arizona	100 to 2000	0.124	0.004	0 320	0 816	0 208	4.426	0.350	0.071	0.000

[1] From Ariz. Agr. Exper. Sta., 24th Ann. Rep., p. 276.
[2] Not including 0.025 per cent $NaHCO_3$.
[3] Not including 0.071 per cent $NaHCO_3$.
[4] Not including 0.033 per cent $NaHCO_3$.
[5] 249.6 parts $CaCO_3$ per 100,000.
[6] 44.0 parts $CaCO_3$ per 100,000.
[7] 15.0 parts $CaCO_3$ per 100,000.
[8] Of the methods compared in this table, only those of the Bureau of Soils, and the New Mexico experiment station distinguish between carbonates and bicarbonates. In soil No. 2 the Bureau of Soils found no carbonates, but 0.071 bicarbonates. Apparently, neither $NaHCO_3$ nor NA_2CO_3 was found by the New Mexico method. The alkalinity obtained by the methods of the other laboratories may have been due to the hydrolysis of some $Mg(HCO_3)_2$, or the results for lime and magnesia may be a little high, so that all bicarbonates were used up by these two metals and none left to combine as $NaHCO_3$ as determined by the New Mexico method.
[9] No carbonates or bicarbonates were found by the Arizona or New Mexico methods in soil No. 3. The alkalinity reported by the methods of other laboratories was in all probability, due to $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$.
[10] 0.604 per cent $CaSO_4$.

It will be seen that the California station uses a proportion of 100 parts of soil to 200 of water, while the Arizona station increases the proportion to 100 parts of soil to 2,000 of water. From the results reported in the

above table, it would seem that increasing the volume of water ten times increases the amount of sodium chlorid dissolved very little, if any. The amount of total solids dissolved is increased, but this may have been due to increased amount of slightly-soluble salts, such as calcium sulphate and calcium and magnesium carbonate. Where total sulphates are calculated to Na_2SO_4, as is done at the California station; and total carbonates to Na_2CO_3, as at the Utah station, a small proportion of water to soil results in the solution of less carbonates of calcium and magnesium and of sulphate of calcium.

The time for treating the soil with water also varies. The Bureau of Soils shakes the mixture 3 minutes and allows it to stand 20 minutes, while by some methods the solution is allowed to stand 24 hours.

Most investigators treat the soil with water at ordinary temperature. The Arizona station heats on a water bath for 10 hours. This is probably to prevent absorption of carbon dioxid and consequent solution of more calcium carbonate and magnesium carbonate. It seems desirable that some experiments be conducted to determine the best temperature and time of treatment. Experiments at the New Mexico station show that the results for carbonates are greater when the solution is filtered through paper than when filtered through the Chamberlain-Pasteur filter. This is due to the more complete removal of suspended particles of insoluble carbonates by the latter method, which should always be used in filtering soil solutions.

TOTAL SOLIDS.

Most investigators determine total solids by evaporating an aliquot of the solution in a platinum dish and drying at 100°C. or more before weighing. According to the Bureau of Soils this determination is "exceedingly unreliable," and by their method "quite unnecessary." They prefer to determine the electrical resistance by means of a Wheatstone bridge, and from this determine the approximate number of ions in the solution.

Practically all other laboratories determine the total solids, which serve as a check on the sum of the total ions determined. In this manner all salts are obtained in a crystalline form, which is often convenient in helping to judge of their character.

CHLORIDS.

Little work seems to be necessary on the chlorin determination. All investigators seem to use standard silver nitrate and the results of different workers on the same solution are fairly concordant.

SULPHATES.

The common method for determining sulphates in soils and waters is by precipitation with barium chlorid. Occasionally the Jackson turbidimeter is used. At some of the laboratories the difference between the total solids and a sum of the chlorids and carbonates is reported as sulphates. The salts of this ion are not always reported.

CARBONATES AND BICARBONATES.

The proper determination of these two radicals and a method to distinguish between their salts as they exist in the soil is most important, since their combination with sodium forms the very injurious black alkali, while the combination of these acid radicals with calcium is a harmless salt. Of the methods now in use in different laboratories one may show black alkali in excess of the toxic limits for crops, while by other methods the same soil may not only indicate the absence of black alkali, but the presence of gypsum, its chemical antidote.

Cameron and others have shown black alkali in the form of bicarbonate to be less toxic than the carbonates, but most investigators fail to distinguish between these two salts on the theory that one form reverts to the other under different field conditions.

At the Utah station[1] the soil solution is titrated directly for carbonates with thirtieth-normal sulphuric acid and the results stated as sodium carbonate. This method would include any carbonates or bicarbonates of lime and magnesia in solution. That the Utah method evidently does include those salts is indicated by the work of Vinson and Catlin shown in Table 1.

It will be seen that this method shows 0.038 per cent sodium carbonate in soil No. 3, which showed no black alkali at all by the Arizona method.

At the California station the soil solution is evaporated to dryness, gently ignited, dissolved in 40 cc. of water, titrated with standard sulphuric acid using methyl orange as the indicator. The results are stated as sodium carbonate. This operation would eliminate some calcium and magnesium salts, but the comparison of methods in the table mentioned in previous paragraph shows that this method may also include small amounts of carbonates or bicarbonates of calcium and magnesium.

The Bureau of Soils attempts to distinguish between carbonates and bicarbonates. For normal carbonates the soil solution is titrated with twentieth-normal potassium acid sulphate until the color from added phenolphthalein is destroyed. For bicarbonates, methyl orange is added

[1] Bulletin No. 121.

to the same solution and titration continued to change of color. While this method has the advantage of distinguishing between carbonates and bicarbonates, it seems to be open to the same criticisms just offered to the Utah and California methods.

At the Arizona station a modification of the Hehner process for permanent hardness is applied to the determination of carbonates. By this process the lime and magnesia salts, if present, are all removed by addition of sodium carbonate of known strength, and the excess titrated with standard acid. This method changes all sodium acid carbonate to sodium carbonate, and fails to distinguish between them. By this method the carbonates of calcium and magnesium are more completely eliminated than by other methods, and the carbonates as determined more nearly represent the true black alkali. This is the method recommended by the association for black alkali in irrigating waters.

The New Mexico station uses the method of the Bureau of Soils for normal carbonates. Cameron has shown that calcium carbonates and magnesium carbonate may hydrolyze and indicate normal carbonates with phenolphthalein, especially in the presence of sodium chlorid and sodium sulphate. Some residues from soil solutions, after repeated washings with hot water, will slowly hydrolyze and react alkaline with phenolphthalein. This has been frequently noted with New Mexico soils.

On the assumption that soluble calcium and magnesium salts are not likely to be found in the presence of black alkali, the New Mexico station has attempted to distinguish the bicarbonates of calcium and magnesium from the sodium salts of this acid by first combining all calcium and magnesium in the soil solution as bicarbonates. The remaining uncombined bicarbonates are calculated to sodium acid carbonate. This necessitates an accurate determination of calcium and magnesium since in calculating these ions to bicarbonates any error for calcium is multiplied by 4, and for magnesium by 6. This is the association method for combining carbonates in water determinations. The New Mexico station has recently compared this method with the Arizona and California methods, somewhat modified, on a number of New Mexico soils. The results, as a rule, show a fairly close agreement between the New Mexico and Arizona methods, but the California method as modified usually gives higher results. The results obtained are reported in Table 2.

CALCIUM AND MAGNESIUM.

These elements are not always determined in an alkali analysis of soils; perhaps not as often as they should be, but when determined the usual well known and reliable methods are used.

TABLE 2.

Comparison of results obtained for black alkali by three different methods.

SOIL NUMBER	NEW MEXICO METHOD[1]		CALIFORNIA METHOD MODIFIED[2]		ARIZONA METHOD MODIFIED[3]	RESULTS BY NEW MEXICO METHOD CALCULATED TO Na_2CO_3	RESULTS BY CALIFORNIA METHOD CALCULATED TO Na_2CO_3
	Sodium carbonate	Sodium acid carbonate	Sodium carbonate	Sodium acid carbonate	Sodium carbonate		
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	0.022	0.191	0.158	0.153	0.153	0.143	0.255
2	0.050	0.187	0.171	0.180	0.204	0.168	0.285
3	0.017	0.175	0.072	0.110	0.178	0.127	0.141
4	0.008	0.000	0.000	0.022	0.000	0.008	0.014
5	0.011	0.000	0.000	0.009	0.000	0.011	0.006
6	0.006	0.000	0.000	0.009	0.000	0.006	0.006
7	0.011	0.211	0.111	0.118	0.170	0.144	0.185
8	0.000	0.048	0.011	0.042	0.042	0.030	0.037
9	0.000	0.018	0.017	0.031	0.017	0.011	0.037
10	0.113	0.176	0.166	0.167	0.233	0.224	0.271
11	0.000	0.119	0.033	0.062	0.098	0.075	0.072
12	0.000	0.077	0.019	0.026	0.042	0.049	0.035
13	0.446	0.015	0.453	......	0.382	0.455	0.453
14	0.000	0.050	0.037	0.048	0.051	0.032	0.067
15	0.204	0.193	0.337	0.289	0.372	0.326	0.519
16	0.050	0.172	0.160	0.160	0.203	0.159	0.261
17	0.000	0.026	0.030	0.033	0.000	0.016	0.051
18	0.017	0.151	0.100	0.063	0.170	0.112	0.140
19	0.017	0.129	0.111	0.063	0.140	0.098	0.151
20	0.003	0.116	0.069	0.105	0.119	0.076	0.135
21	0.000	0.000	0.044	0.000	0.000	0.000	0.044
22	0.006	0.138	0.110	0.101	0.110	0.093	0.174
23	0.000	0.000	0.000	0.000	0.017	0.000	0.000
24	0.260	0.205	0.350	0.319	0.390	0.389	0.551
25	0.032	0.178	0.276	0.231	0.195	0.144	0.422
26	0.005	0.065	0.064	0.071	0.092	0.016	0.109
27	0.000	0.120	0.064	0.059	0.092	0.076	0.101
28	0.482	0.083	0.482	0.403	0.492	0.534	0.736
29	0.196	0.204	0.307	0.286	0.297	0.325	0.487
30	0.000	0.171	0.106	0.126	0.110	0.108	0.185
31	0.016	0.218	0.159	0.164	0.187	0.154	0.162
32	0.056	0.222	0.180	0.172	0.246	0.196	0.289
33	0.201	0.223	0.329	0.294	0.424	0.342	0.514
34	0.536	0.365	0.562	0.479	0.806	0.765	0.864
35	0.000	0.212	0.127	0.172	0.161	0.134	0.235
36	0.037	0.080	0.095	0.092	0.119	0.087	0.153
37	0.111	0.069	0.159	0.151	0.195	0.155	0.254
38	0.011	0.014	0.019	0.040	0.034	0.020	0.044
39	0.037	0.120	0.118	0.024	0.102	0.113	0.133
40	0.016	0.112	0.088	0.004	0.085	0.087	0.091
41—							
1st foot	0.311	0.209	....	....	0.508	0.443	....
2d foot	0.311	0.209	....	....	0.480	0.443	....
3d foot	0.286	0.201	....	....	0.449	0.413	....
4th foot	0.286	0.201	....	....	0.415	0.413	....

[1] Association method for irrigating waters.

[2] By this method the soil filtrate was evaporated, gently ignited, redissolved in freshly-boiled water, and titrated for CO_3 and HCO_3 with $KHSO_4$.

[3] Association method for "black alkali."

SODIUM.

This element is not often determined because the usual process for its determination is too long. Some laboratories report the difference between the total solids and the sum of the other substances determined as sodium. At the New Mexico station the sodium reported is a sum of the sodium ions in the salts calculated in probable combination with the acid ions.

STATEMENT OF RESULTS.

It is essential that the results of alkali investigations be expressed in a uniform manner, and in form most readily interpreted by the public.

Some investigators report their results as radicals, others give only partial probable combinations, while in some cases a complete combination of all of the acid and basic radicals is attempted.

The Bureau of Soils[1] combines all Ca, Mg, K and Na with SO_4, Cl, CO_3 and HCO_3 in the order named. They say that "convenience justifies such a combination, which is arbitrary, although sometimes a source of "much useful information."

This method of combination may indicate sodium carbonate and sodium acid carbonate in the same solution with calcium sulphate and in amounts sufficient to exceed the usually accepted toxic limits of crops. This bureau, in a recent bulletin on the "Soil Survey of the Middle Rio Grande Valley Area, New Mexico," reports 738 parts of sodium acid carbonate, 84 parts sodium carbonate and 3376 parts of calcium sulphate per 100,000 parts of alkali. The carbonate and bicarbonate radicals determined in these samples were probably combined with calcium and magnesium ions.

At the Utah station both carbonates and bicarbonates are reported as sodium carbonate, all chlorin as sodium chlorid, and all calcium as calcium sulphate. Bulletin No. 121 of this station gives analyses of radicals combined in this manner which show as much as 0.1 per cent sodium carbonate in solution with 2.34 per cent calcium sulphate. The California station reports all carbonates and bicarbonates as sodium carbonate.

At the Arizona station carbonates, chlorids and permanent hardness are determined and reported as sodium carbonate, sodium chlorid, and calcium sulphate, respectively.

The method recommended by the association for combining the radicals in irrigating waters is used at the New Mexico station. All calcium and magnesium are calculated to the acid ions in the following order: HCO_3, SO_4, and Cl: then the remaining acid ions, including CO_3, are calculated to the corresponding Na salts.

[1] Seidell: Chemical Examination of Alkali Soils.

In a circular from the Bureau of Plant Industry, on the "Work of Truckee-Carson Reclamation Project Experimental Farm," on page 11 they state that it is "sufficiently accurate to calculate all analyses to sodium salts." By calculating all carbonates and bicarbonates to sodium salts, nearly all soil solutions would contain enough black alkali to condemn them if we accept 0.05 per cent as the toxic quantity.

No report was made by the referee on inorganic plant constituents.

The meeting adjourned at 12.30 to convene for the afternoon session at 2.

MONDAY—AFTERNOON SESSION.

At the opening of the afternoon session, the following committees were announced by the president:

Committee to invite the Secretary or the Assistant Secretary to address the association: P. F. Trowbridge, of Missouri; R. N. Brackett, of South Carolina; and C. B. Lipman, of California.

Committee on resolutions: William Frear, of Pennsylvania; B. B. Ross, of Alabama; and H. H. Hanson, of Maine.

Auditing committee: R. J. Davidson, of Virginia; H. B. McDonnell, of Maryland; and R. E. Stallings, of Georgia.

Committee on nominations: W. A. Withers, of North Carolina; H. C. Lythgoe, of Massachusetts; and A. J. Patten, of Michigan.

REPORT ON INSECTICIDES.

By R. C. Roark (Bureau of Chemistry, Washington, D. C.) *Referee.*

The coöperative work on insecticides this year has included the study of methods for the determination of moisture, carbon dioxid, copper, arsenic and lead oxid as they occur in one or more of the following: Bordeaux, Bordeaux-lead arsenate, and Bordeaux-Paris green. Work was also done on the comparison of new methods for the determination of nicotin, and of arsenious oxid in Paris green, with the present official methods.

In the spring the following letter was sent to the chemists of eighteen experiment stations:

Dear Sir: I am writing to ask if you will coöperate in the A. O. A. C. work on insecticides this year.

The association at its last meeting recommended that the following methods be studied: (1) Hedges' method for the determination of arsenious oxid in Paris green and other insecticides (J. Ind. Eng. Chem., 1909, **1**: 208); and (2) the Lloyd method for the determination of nicotin in tobacco and tobacco extracts (Bur. Chem. Bul. 56, p. 114).

In addition, in view of the wide use of Bordeaux mixture and the fact that no methods for its analysis have been adopted, it is proposed to study methods for the determination of the principal ingredients of Bordeaux, Bordeaux-lead arsenate and Bordeaux-Paris green mixtures. Furthermore, the silicotungstate method for the determination of nicotin (B. A. I. Bul. 133) has been used with entire

satisfaction in this laboratory for nearly three years, and I should like to have it tested by the collaborators.

The work on insecticides for 1914, therefore, will comprise a study of the following:

(1) The Lloyd and silicotungstate methods for the determination of nicotin.

(2) Methods for the determination of moisture, carbon dioxid, copper, lead and arsenic as they occur in one or more of the following: Bordeaux, Bordeaux-lead arsenate, and Bordeaux-Paris green.

(3) Hedges' method for the determination of arsenious oxid in Paris green.

Of the eighteen stations, four did not reply, five were not able to coöperate, while nine promised to assist in the work, but of these latter two have not sent in any results. Two analysts from California and three from Minnesota sent in results. Six analysts from the Insecticide and Fungicide Laboratory of the Bureau of Chemistry have assisted in certain determinations, so that altogether sixteen chemists have coöperated in the work for this year.

The directions sent the coöperators were as follows:

INSTRUCTIONS TO COLLABORATORS.

HEDGES METHOD FOR ARSENIOUS OXID IN PARIS GREEN.

Place 2 grams of the sample in a 250 cc. graduated flask and dissolve in about 50 cc. of hydrochloric acid (1 : 1) by warming on the steam bath at a temperature of not over 80° C. When completely dissolved cool and make to mark with distilled water. Pipette a 25 cc. aliquot into an Erlenmeyer flask, dilute to about 300 cc. add a sufficient excess of sodium bicarbonate to dissolve the precipitate which is first formed and titrate with twentieth-normal iodin solution with starch paste as an indicator. The color change indicating the end point may be best observed against a white background. (The original directions call for the titration to be made in a porcelain evaporating dish.) The titration (with twentieth-normal iodin solution should not be made until all the copper carbonate which is precipitated by the sodium bicarbonate has been redissolved by an excess of that reagent. Ten to 15 grams of sodium bicarbonate will be sufficient in most cases).

C. M. SMITH METHOD FOR ARSENIOUS OXID IN PARIS GREEN.

Transfer 2 grams of the sample to a 250 cc. graduated flask, add 50 cc. of water and 50 cc. of sulphuric acid (1: 4), warming on the steam bath until solution is complete. Cool and make to mark with distilled water. Pipette a 25 cc. aliquot into a 500 cc. Erlenmeyer flask, dilute to about 150 to 200 cc., neutralize with sodium bicarbonate, and add about 10 grams in excess. Then add about 5 grams of ammonium chlorid, which will dissolve the copper carbonate. Titrate as usual with twentieth-normal iodin, with starch paste as an indicator.

A blank should be run using an equivalent weight of copper sulphate, and this blank which should never be over 0.2 cc., subtracted from the titration reading.

BORDEAUX MIXTURE.

(1) *Moisture.*—(a) If the sample is in the form of a powder, dry 2 grams to constant weight at 105°–110° in an oven and report the percentage lost as moisture.

(b) If the sample is in the form of a paste, heat a weighed portion of about 100 grams in an oven at 90° to 100° until dry enough to powder readily, and note the loss in weight. Determine carbon dioxid both on the original paste and on this rough dried sample according to the method described under (2). Powder this rough dried sample, weigh out about 2 grams and determine remaining moisture as under (a). Calculate total moisture as follows: Total moisture = loss on first drying plus (1 − loss on first drying) (loss on second drying + carbon dioxid in dried sample) —carbon dioxid in paste.

(2) *Carbon dioxid.*—Determine carbon dioxid on 2 grams of the powder according to the method of Fresenius (U. S. Geol. Survey Bul. 422, pp. 179–181; Fresenius, Quantitative Chemical Analysis, 1911, **2**: 1180). In the case of a paste, use about 10 grams, which should be weighed out in a stoppered flask.

(3) *Copper.*—(a) Treat 2 grams of the dry powdered sample with 20 cc. of water and 5 cc. of concentrated nitric acid, dilute to 100 cc. and wash into a weighed platinum dish of about 150 cc. capacity, and electrolyze, using a rotating spiral anode with a current of about 2 amperes and 3 to 4 volts. After all the copper is deposited (which should take about one-half hour) wash the deposit by siphoning with distilled water, then rinse with alcohol, dry for a few minutes in an oven, and weigh.

(b) Dissolve 2 grams of the dry powdered sample in about 50 to 100 cc. of 10 per cent nitric acid, add ammonium hydroxid in excess and heat, and filter off any iron that may be present. Wash precipitate thoroughly, boil off excess of ammonia from filtrate, add 5 to 10 cc. of acetic acid, cool, add 3 grams of potassium iodid and titrate with standard thiosulphate solution.

The thiosulphate solution used for this titration should be standardized exactly as described on page 241 of Bureau of Chemistry Bulletin 107, Revised. In determining the copper in a Bordeaux, however, the use of bromin is not necessary, as no oxids of nitrogen are formed in dissolving the sample.

Calculate all results to original material.

BORDEAUX MIXTURE WITH PARIS GREEN.

(1) *Moisture.*—Determine as directed for Bordeaux mixture.

(2) *Carbon dioxid.*—Determine as directed for Bordeaux mixture.

(3) *Copper.*—(a) Dissolve 2 grams of the dry powdered sample in a few cc. of strong nitric acid, add 25 cc. of a 3 per cent solution of hydrogen peroxid and warm for 5 to 10 minutes. Make slightly alkaline with ammonium hydroxid, then slightly acid again with dilute nitric acid. Transfer to a weighed platinum dish of about 150 cc. capacity, add 15 to 20 cc. more hydrogen peroxid, dilute to 100 cc. and electrolyze with a current not exceeding 2 amperes, using a rotating spiral anode. After the electrolysis has proceeded for about 20 minutes, add to the electrolyte 0.5 grams of ferric sulphate dissolved in a few cubic centimeters of water together with a drop or two of nitric acid. After all the copper is deposited wash the deposit by siphoning with distilled water, then rinse with alcohol, dry for a few minutes in an oven, and weigh. (Do not pass the current for more than 5 to 10 minutes after all the copper has been deposited without adding more ferric sulphate.)

(b) Weigh 2 grams of the dry powdered sample into a casserole or porcelain evaporating dish, add 25 cc. of fuming nitric acid and evaporate to dryness. Now add 5 cc. of concentrated sulphuric acid and heat to appearance of white fumes. Dilute with water, heat, add ammonium hydroxid, filter off calcium sulphate and iron, if present, and proceed as directed for the volumetric determination of copper under Bordeaux mixture.

(4) *Arsenious oxid* (As_2O_3).—Determine by distillation with hydrochloric acid as given under BORDEAUX MIXTURE WITH LEAD ARSENATE, using 0.5 gram material for the determination.

(5) *Water-soluble arsenious oxid* (As_2O_3).—Treat 2 grams with 1,000 cc. of distilled water, digesting for 24 hours at a temperature of 32°C., shaking 8 times during the day at intervals of 1 hour. Filter through a dry filter, take a 250 cc. aliquot, make slightly acid with hydrochloric acid (methyl orange as indicator), then alkaline with excess of sodium bicarbonate, and titrate with twentieth-normal iodin as usual. Make corrections for iodin necessary to produce the same color using same chemicals and same volume.

Calculate all results to original material.

BORDEAUX MIXTURE WITH LEAD ARSENATE.

(1) *Moisture.*—Determine as directed for BORDEAUX MIXTURE.

(2) *Carbon dioxid.*—Determine as directed for BORDEAUX MIXTURE.

(3) *Copper.*—Treat one gram of the dry powdered sample with 20 cc. of water and 5 to 6 cc. of concentrated nitric acid, heat to boiling, cool, and add concentrated ammonium hydroxid to slight excess. Wash the solution, together with the precipitate, into a weighed platinum dish of about 150 cc. capacity, and electrolyze, using a rotating anode and a current of about 4 amperes and 3 to 4 volts for about one and one-half hours (or until the copper is all deposited). Wash the deposit by siphoning until the deposit is clean, being careful not to use too much wash water. Redissolve the copper in 5 cc. of concentrated nitric acid, make the solution to 100 cc. and electrolyze as before, except that all the copper will be deposited in a half hour. Wash the deposit by siphoning with distilled water, then rinse with alcohol, dry for a minute or so in an oven and weigh.

(4) *Lead oxid.*—Dissolve the lead peroxid, together with a little arsenic, from the anode used in the copper electrolysis by means of dilute nitric acid and a little hydrogen peroxid and add to the washings from both electrolyses of copper. Add ammonium chlorid to dissolve any lead sulphate which may have precipitated out and make the solution to 1,000 cc. Pipette 200 cc. of this into a 400 cc. beaker, dilute to about 300 cc., and precipitate the lead as lead chromate, according to the method for lead oxid in lead arsenate (Bur. Chem. Bul. 152, p. 68).

Total arsenic oxid (As_2O_5).—Weigh into a distilling flask 0.5 gram of the dry powder, add about 10 grams of ferrous sulphate and 100 cc. of concentrated hydrochloric acid. Distill through a well-cooled condenser and adapter into a 700 cc. Erlenmeyer flask containing about 100 cc. of water. When volume in the distilling flask equals about 40 cc., add 50 cc. more concentrated hydrochloric acid by means of a dropping funnel and continue distillation. Repeat until a freshly-distilled portion contains no more than traces of arsenic (tested by neutralizing with sodium bicarbonate and adding iodin solution together with a little starch paste). Nearly neutralize the distillates with 25 per cent sodium hydroxid solution, using methyl orange as an indicator, being careful to keep the solution well cooled. If the neutral point is passed, add hydrochloric acid until acid again. Make alkaline with sodium bicarbonate and titrate with standard iodin solution using starch paste as an indicator.

(6) *Water-soluble arsenic oxid* (As_2O_5).—Determine according to the method for the determination of water-soluble arsenic oxid in lead arsenate recommended for provisional adoption by the association in 1913, which is as follows: Weigh to 0.01 gram about 4 grams of paste. Place in a tightly-stoppered flask or bottle with 250 cc. of freshly-boiled and cooled distilled water per gram and keep at 32° C. for 24

hours, shaking well every hour during the working day (8 times in all), filtering at the end of 24 hours. Use 250 cc. of the clear filtrate for the determination. Add 0.5 cc. of sulphuric acid and proceed as directed under water-soluble arsenic oxid, Bulletin 107, Revised, p. 240. It is important that the solution shall be perfectly clear and the titrations carefully made. Make corrections for iodin necessary to produce the same color, using same chemicals and volume.

Calculate all results to original material.

SILICOTUNGSTIC ACID METHOD FOR NICOTIN.

There are several silicotungstic acids. For use in this method the silicoduodecitungstic acid of the formula $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$ should be employed. The acids $4H_2O \cdot SiO_2 \cdot 10WO_3 \cdot 3H_2O$ and $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 20H_2O$, do not give crystalline precipitates with nicotin and should not be used in this method. Merck and Company's silicotungstic acid cryst. has been found satisfactory.

(a) Weigh out such an amount of the preparation as will contain preferably between 0.1 and 1.0 gram of nicotin (in the case of samples containing very little nicotin, about 0.1 per cent; the amount of sample must not be increased to the point where it interferes with the distillation); wash with water into a 500 cc. round-bottomed flask; add a little paraffin to prevent frothing, a few small pieces of pumice and a slight excess of 1 to 2 sodium or potassium hydroxid solution, using phenolphthalein as an indicator. Distill in a rapid current of steam through a well-cooled condenser, and adapter, into 10 cc. of dilute hydrochloric acid (1 : 4) in a capacious flask. When distillation is well started, apply heat to the distillation flask to reduce the volume of the liquid as far as practicable without bumping or undue separation of insoluble matter. Continue distillation until a few cubic centimeters of the distillate collected from the condenser after removal of the adapter show no cloud or opalescence when treated with a drop of silicotungstic acid solution followed by a drop of dilute hydrochloric acid (1 : 4). Prove alkalinity of the residue in the distillation flask with phenolphthalein solution. Make the distillate, which may amount to 1,000 to 1,500 cc. to convenient volume, mix well and pass through a large dry filter if not clear. Test a portion with methyl orange to assure its acidity. Pipette into a beaker an aliquot containing about 0.1 gram nicotin (in the case of samples containing very small amounts of nicotin, an aliquot containing as little as 0.01 gram of nicotin may be used), add to each 100 cc. of liquid 3 cc. of dilute hydrochloric acid (1 : 4), or more if indicated necessary by the test with methyl orange, and add 1 cc. of a 12 per cent solution of silicotungstic acid for each 0.01 gram of nicotin supposed to be present. Stir thoroughly and let stand overnight. Before filtering, stir up the precipitate to see that it settles quickly and is in crystalline form; then filter on a prepared Gooch which has been dried to constant weight at 125° C., and wash with cold water acidulated with hydrochloric acid (1 cc. of concentrated acid per liter). Dry to constant weight at 125°C., and from weight of anhydrous nicotin silicotungstate calculate nicotin, using the factor, weight nicotin silicotungstate $\times$ 0.1012 = weight nicotin. (As dried nicotin silicotungstate is very hygroscopic, in weighing the Gooch crucibles they should always be inclosed in a weighing bottle with glass stopper to avoid contact with the air.)

(b) Proceed as directed under (a) except filter on a quantitative paper filter, wash as before, transfer paper and precipitate to a weighed platinum crucible, dry carefully, and ignite until all carbon is consumed. Finally heat for not more than ten minutes over a Teclu or Meker burner. Calculate nicotin as follows: Weight residue $\times$ 0.114 = weight nicotin.

LLOYD METHOD FOR NICOTIN.

Weigh out carefully such a quantity of the material that the amount of nicotin present will be from 0.05 to 0.50 gram. Add 2 cc. of a 10 per cent solution of ferric chlorid for each gram of sample, and mix well. In the case of powders, add enough water to make a thin pasty mass. Now add, with stirring, enough solid sodium bicarbonate to form a stiff paste. After thoroughly mixing in the sodium bicarbonate, which should be present in excess, extract the mass 10 times with petroleum ether, using 20 cc. each time. This extraction should be carried out very thoroughly, care being taken that all parts of the mass are reached by the solvent. Put all the petroleum ether extracts in a separatory funnel, and extract 3 times with tenth-normal sulphuric acid, using 20 cc. each time. Extract twice more with water, using 20 cc. for each extraction, combine the acid and aqueous extracts, and titrate with tenth-normal sodium or potassium hydroxid, with litmus as an indicator. Each cubic centimeter of tenth-normal sulphuric acid not titrated by the alkali equals 0.01621 gram of nicotin.

In order to thoroughly test these methods, the following representative samples were used:

Paris green—commercial.

Bordeaux powder—commercial.

Bordeaux paste—prepared in the Insecticide and Fungicide Laboratory.

Bordeaux-Paris green—commercial powder.

Bordeaux-lead arsenate—commercial paste.

Tobacco powder—commercial.

Nicotin solution No. 1—commercial concentrated solution.

Nicotin solution No. 2—prepared by diluting solution No. 1 and adding a little pyridin and ammonium chlorid.

C. M. Smith's method for the determination of arsenious oxid in Paris green was included in the directions sent the coöperators, as it had been tested in the Insecticide and Fungicide Laboratory and found to be quick and accurate.

ANALYTICAL RESULTS OF THE COÖPERATORS.

PARIS GREEN.

Below are tabulated the results obtained by the coöperating chemists on the sample of Paris green as analyzed according to the different methods:

Anaylsis of Paris green.
(Results expressed as per cent.)

ANALYST	TOTAL ARSENIOUS OXID (As_2O_3)			
	Official method	Modified official method	C. M. Smith method	C. C. Hedges method
A. K. Anderson, Minnesota	60.54 59.80 59.72	....	58.34 58.41	59.61 59.94 ....
Average	60.02	....	58.38	59.78
J. J. Willaman, Minnesota	59.51 60.33 58.90	....	56.85 57.07	60.29 59.73 60.02
Average	59.58	....	56.96	60.01
C. M. Smith, Washington, D. C.	58.35 58.35 58.32 58.14	58.35 58.29 58.23 58.42	57.80 57.80 57.80 57.86	57.92 57.86 57.80 57.80
Average	58.29	58.32	57.82	57.85
W. B. Ellett and W. G. Harris, Virginia	59.47 59.17 60.10	....	58.41 58.41 58.79 58.29 58.66	58.91 58.78 58.41 58.79 58.79
Average	59.58	....	58.51	58.74
J. J. T. Graham, Washington, D. C.	58.32 58.18 58.18	58.14 58.39 58.14	58.11 58.04 58.04	[1]58.07 [1]58.00 [1]58.03
Average	58.23	58.22	58.06	58.03
O. B. Winter, Michigan	58.74 58.93	....	58.50 58.50	58.69 58.45
Average	58.84	....	58.50	58.57
Geo. P. Gray, California	....	....	57.23 57.54 57.78 57.78	57.87 57.84 57.87 57.96
Average	....	....	57.58	57.89
S. D. Averitt, Kentucky	....	....	57.87 57.87 57.87	57.93 57.87 57.87
Average	....	....	57.87	57.89

[1] Run at 60° instead of 80°.

Analysis of Paris green.—Concluded.

ANALYST	TOTAL ARSENIOUS OXID (As_2O_3)			
	Official method	Modified official method	C. M. Smith method	C. C. Hedges method
E. R. Tobey, Maine	58.56	....	59.41	58.07
	58.62	....	59.29	58.19
	....	....	59.29	58.07
Average	58.59	....	59.33	58.11
F. L. Elliott, Washington, D. C.	58.67	58.57	58.11	57.62
	58.60	58.53	58.15	57.62
	58.50	58.50	58.15	57.57
Average	58.59	58.53	58.14	57.60
R. C. Roark, Washington, D. C.	58.50	....	57.94	57.94
	....	....	57.94	57.87
	58.65	....	57.94	57.72
	58.50	....	57.94	57.72
	58.43	....	57.94	57.72
	58.43	....	57.94	57.72
Average	58.50	....	57.94	57.78

The official method in the above table is the method given on page 25 of Bulletin 107, Revised, of the Bureau of Chemistry. The modified official method is the same except that sulphuric acid is substituted for hydrochloric in the reduction of arsenic oxid by potassium iodid and acid. This modified official method is essentially the method used in determining arsenic oxid in lead arsenate (Bur. Chem. Bul. 107, Rev., p. 239).

The following comments by the coöperators on these methods are of interest:

COMMENTS BY ANALYSTS.

E. R. Tobey: Much prefer Hedges method to the C. M. Smith method, or even the official.

S. D. Averitt (Speaking of the method of Hedges and Smith): The results show that one method is as good as the other and the method used might be left to the choice of the worker.

O. B. Winter: The Smith and Hedges methods consume less time than the official method, but run slightly lower. This latter is probably due to a small amount of arsenic oxid present which is reduced by the potassium iodid in the official method.

J. J. T. Graham and F. L. Elliott: Much prefer the Smith method to the Hedges method, as there is no danger of losing any arsenic when a Paris green is dissolved in sulphuric acid, whereas when hydrochloric acid is used as in the Hedges method the temperature must be closely watched or some arsenious chlorid will be lost.

It will be noted that the results of the different analysts do not agree as closely as might be expected, even those results obtained by the official

method varying nearly 2.0 per cent. This is probably due partly to errors in standardizing the iodin solution. Very few samples of arsenious oxid are 100 per cent pure and a slight error in the value of the iodin solution introduces a considerable error in the determination.

As a rule the results by the Hedges method are a trifle lower than those by the official method. This is most likely due to the escape of a part of the arsenic as arsenious chlorid. If the temperature is kept at 60° instead of 80° better results are obtained. In C. M. Smith's method the results are generally lower than those obtained by the official method. In analyzing a sample of Paris green according to this method the following precautions should be observed: The Paris green must be completely dissolved in the acid; the precipitate caused by the addition of the sodium bicarbonate must be completely redissolved by the addition of ammonium chlorid; and the blue color produced by the action of iodin on starch must not be confused with the blue color of the solution. When ammonium chlorid is added the blue color is darker than when only sodium bicarbonate is used, but with a little experience the end point of the iodin titration may be determined as sharply as in a colorless solution. The methods of Smith and Hedges are found to yield better results if modified as given on page 446 of this report. The following table gives results obtained by these two methods as sent to the coöperators, and as modified on page 446.

Total arsenious oxid (As_2O_3) *by modified and unmodified methods.*

ANALYST	SMITH METHOD		HEDGES METHOD	
	Original	Modified	Original	Modified
	per cent	*per cent*	*per cent*	*per cent*
R. C. Roark, Washington, D. C.	57.94	58.55	57.94	58.50
	57.94	58.50	57.87	58.35
	57.94	58.55	57.72	58.65
	57.94	58.60	57.72	58.65
	57.94	58.50	57.72	....
	57.94	.....	57.72	.....
Average	57.94	58.54	57.78	58.54
F. L. Elliott, Washington, D. C.	58.11	58.15	57.62	58.15
	58.15	58.15	57.62	58.10
	58.15	58.10	57.57	58.10
Average	58.14	58.13	57.60	58.12
C. M. Smith, Washington, D. C.	57.80	58.10	57.92	[1]58.00
	57.80	58.10	57.86	[1]58.20
	57.80	58.15	57.80	....
	57.86	58.25	57.80	....
Average	57.82	58.15	57.85	58.10

[1] Dissolved at room temperature.

In these methods as modified, more acid in proportion to the weight of sample is used, thus insuring a complete decomposition of the Paris green.

Both the methods of Hedges and C. M. Smith are easy, quick, and accurate ones for the determination of arsenious oxid (As_2O_3) in Paris green, but they are not applicable for the determination of total arsenic where part of it is in the form of arsenate. Paris green, however, should not contain arsenic in this form.

In the official method the use of sulphuric instead of hydrochloric acid has the following advantages:

(1) There is no danger of losing arsenic as arsenious chlorid, the reduction of As_2O_5 to As_2O_3 is always complete, and the method yields more closely-agreeing results with less care in manipulation.

(2) Less acid and less potassium iodid are required, therefore the method is cheaper as regards reagents, and less time is required for neutralizing the acid.

The method of determining arsenic by distillation with hydrochloric acid is a very accurate one, and although not tried out on a straight Paris green, it has been used in the case of Bordeaux-Paris green and Bordeaux-lead arsenate mixtures with entire satisfaction.

I, therefore, recommend that these methods, as given in the following paragraphs, be adopted as official and that the present methods for the determination of total arsenious oxid in Paris green, as published in Bureau of Chemistry Bulletin 107, Revised, pages 25 to 27, be discarded.

METHODS FOR PARIS GREEN.

Total Arsenic Present as As_2O_3 *and* As_2O_5

SOLUTIONS REQUIRED:

Starch solution.—Use a starch solution prepared as follows: Stir finely-powdered potato starch in a small amount of cold distilled water until a uniform suspension results, then slowly add this suspension, with constant stirring, to boiling distilled water. About 0.5 gram of starch to each 100 cc. of the completed solution should be used. After the starch suspension is added to the boiling water the heating should be discontinued.

Standard solution of arsenious oxid (As_2O_3).—Chemically pure arsenious oxid, which should be carefully tested for impurities according to the methods of Krauch, should be used. Prepare a solution of the arsenious oxid of such strength that 50 cc. of it contain 0.2000 gram, in one of the following ways:

(a) Dissolve, without heating, in a freshly-prepared solution of chemically pure sodium or potassium hydroxid, using 4 to 5 grams of the alkali to each gram of the arsenious oxid.

(b) Dissolve by boiling in a 12 to 15 per cent solution of sodium bicarbonate, using about 6 grams of the sodium bicarbonate to each gram of the arsenious oxid.

(c) Dissolve by boiling in water containing about 4 or 5 grams of sulphuric acid per gram of arsenious oxid present.

(d) Dissolve in a 10 per cent solution of hydrochloric acid by warming on the steam bath, being careful that the temperature does not exceed 60° C.

After solution is effected in one of the above ways, the solution should be cooled and made up to volume in a graduated flask.

Standard iodin solution.—Prepare an approximately twentieth-normal solution of iodin as follows: Intimately mix chemically pure powdered iodin with twice its weight of chemically pure potassium iodid, uisng 6.35 grams of the iodin for each liter of solution desired. Make up to volume and standardize as follows: Pipette into an Erlenmeyer flask 50 cc. of the standard solution of arsenious oxid, which, if prepared according to methods (a) or (b), should then be acidified with either hydrochloric or sulphuric acid. Neutralize with sodium bicarbonate, adding 4 or 5 grams in excess, and add from a pipette 50 cc. of the standard iodin solution. Now add about 5 cc. of the starch solution, and run in the iodin solution drop by drop from a burette until a permanent blue color is obtained. From the number of cubic centimeters of iodin used should be deducted the number of cubic centimeters of iodin necessary to produce the same intensity of color in a solution of the same reagents (except arsenic) and of the same volume. From the corrected number of cubic centimeters of iodin calculate the value of the iodin solution in terms of arsenious oxid (As_2O_3).

DETERMINATION:

Method I.

Weigh carefully an amount of Paris green such that when dissolved and made up to volume in a graduated flask 50 cc. of the solution will contain an amount of Paris green equal to the amount of arsenious oxid to which 100 cc. of the iodin solution are equivalent. (Example.—If 1 cc. of the standard iodin solution = 0.002841 gram of As_2O_3, weigh $5 \times 0.2841 = 1.4205$ gram Paris green and when dissolved make up to volume in a 250 cc. flask). Transfer the Paris green to the graduated flask by means of about 100 cc. of a 2 per cent sodium hydroxid solution and boil the mixture thoroughly until no green particles are visible. Cool and make up to volume. Filter the well-shaken liquid through a dry filter and use 50 cc. portions for analysis. Pipette 50 cc. into an Erlenmeyer flask, dilute to about 100 cc. with water, add 3 to 4 cc. of concentrated sulphuric acid and 1 gram of potassium iodid and boil down to 40 cc. Cool under running water, and add approximately twentieth-normal thiosulphate solution drop by drop from a burette until the solution is exactly colorless. Add sodium bicarbonate in excess and titrate with the standard iodin solution as directed under standardization. The corrected number of cubic centimeters of iodin used in this titration represents directly the total per cent of arsenic in the sample expressed as As_2O_3. (If any arsenic should be present in the form of arsenate it will be titrated as As_2O_3 according to this method.)

Method II.

Weigh carefully an amount of Paris green equal to the amount of arsenious oxid to which 100 cc. of the standard iodin solution are equivalent, and wash into a distilling flask by means of 100 cc. of concentrated hydrochloric acid. Add about 5 grams of ferrous sulphate and distill through a well-cooled condenser and adapter into a large Erlenmeyer flask containing about 50 to 100 cc. of water. When the volume in the distilling flask equals about 40 cc., add 50 cc. more concentrated hydrochloric acid by means of a dropping funnel and continue distillation. Repeat until a freshly-distilled portion contains no more than traces of arsenic (tested by neutralizing with sodium bicarbonate, adding a little starch paste and a few drops of iodin solution). Nearly neutralize the distillates with 25 per cent sodium hydroxid solution, using methyl orange as an indicator, being careful to keep the solution well

cooled. (If the neutral point is passed, add hydrochloric acid until acid again.) Add sodium bicarbonate in excess and titrate with standard iodin solution as directed in *Method I*.

Total Arsenic Present as As_2O_3 *Only.*

Method III.

(a) *Procedure of C. C. Hedges, modified.*—Weigh carefully an amount of Paris green equal to the amount of arsenious oxid to which 100 cc. of the iodin solution are equivalent, wash into an Erlenmeyer flask by means of about 25 to 30 cc. of 1 to 1 hydrochloric acid followed by about 100 cc. of water, and heat on the steam bath only as long as is necessary to complete solution, being careful that the temperature of the solution does not exceed 60°C. Cool, neutralize with sodium bicarbonate, adding an excess, and add sufficient ammonium chlorid to dissolve the copper which is precipitated. Dilute somewhat, and add 50 cc. of iodin solution from the same pipette used in standardizing, then add about 5 cc. of the starch solution and finish the titration as directed under standardization. The corrected number of cubic centimeters of iodin used in this titration represents directly the per cent of arsenious oxid (As_2O_3) in the sample.

(b) *Procedure of C. M. Smith, modified.*—Proceed as directed above, using 1 to 4 sulphuric acid instead of 1 to 1 hydrochloric. The solution in this case may be heated to boiling.

Total Arsenic Present as As_2O_5 *Only.*

As_2O_3 determined by *Methods I* or *II* minus As_2O_3 determined by *Method III* equals the As_2O_3 really present as As_2O_5.

$As_2O_3 \times 1.16168 = As_2O_5$.

BORDEAUX.

The results obtained on the two Bordeaux mixtures were as follows:

Analysis of Bordeaux mixtures.

SAMPLE AND ANALYST	MOISTURE	CARBON DIOXID	COPPER (ELECTROLYTIC)	COPPER (THIOSULPHATE)
DRY BORDEAUX:	*per cent*	*per cent*	*per cent*	*per cent*
W. B. Ellett and H. H. Hill, Virginia.	....	....	....	13.65
	....	....	....	13.65
	....	....	....	13.65
	....	....	....	13.80
	....	....	....	13.75
Average........	....	....	....	13.70
O. B. Winter, Michigan........	6.94	5.68	....	13.16
	6.98	5.56	....	13.26
	....	5.67	....	13.21
Average........	6.96	5.64	....	13.21
E. L. Griffin, Washington, D. C......	7.59	5.83	13.50	13.55
	7.56	5.85	13.47	13.57
Average........	7.58	5.84	13.49	13.56

Analysis of Bordeaux mixtures.—Concluded.

SAMPLE AND ANALYST	MOISTURE	CARBON DIOXID	COPPER (ELECTROLYTIC)	COPPER (THIOSULPHATE
DRY BORDEAUX:	*per cent*	*per cent*	*per cent*	*per cent*
Geo. P. Koch, Minnesota..........	5.02	5.63	....	12.62
	4.93	5.66	....	12.62
	....	5.63	....	12.58
	....	....	....	12.62
Average..........................	4.98	5.64	....	12.61
E. R. Tobey, Maine................	5.97	5.84	13.44	13.55
	....	....	13.57	13.97
	....	....	....	13.73
	....	....	....	13.63
Average..........................	5.97	5.84	13.51	13.72
R. C. Roark, Washington, D. C.....	7.58	5.75	13.46	13.47
	....	5.85	13.48	13.45
	....	....	....	13.47
Average..........................	7.58	5.80	13.47	13.46

SAMPLE AND ANALYST	MOISTURE	CARBON DIOXID	COPPER (ELECTROLYTIC)	COPPER (THIOSULPHATE)
BORDEAUX PASTE:	*per cent*	*per cent*	*per cent*	*per cent*
O. B. Winter, Michigan............	70.46	0.28	....	5.21
	....	0.26	....	5.26
Average..........................	70.46	0.27	....	5.24
Geo. P. Koch, Minnesota..........	67.18	0.43	....	....
	....	0.46	....	....
	....	0.38	....	....
Average..........................	67.18	0.42	....	....
E. R. Tobey, Maine................	67.88	0.40	5.70	5.89
	....	0.54	5.76	5.81
Average..........................	67.88	0.47	5.73	5.85
R. C. Roark, Washington, D. C....	69.71	0.23	5.52	5.48
	....	....	5.44	5.41
Average..........................	69.71	0.23	5.48	5.45

The coöperating chemists comment as follows on the methods for Bordeaux:

COMMENTS BY ANALYSTS.

O. B. Winter: We have no apparatus for estimating copper electrolytically so have omitted the electrolytic method. The above methods on dry Bordeaux were found very satisfactory.

E. R. Tobey: Experienced some difficulty in fixing the end point in determining copper by the titration method, and prefer the electrolytic method.

The above figures show that very good results were obtained by the analysts. Outside of the Insecticide and Fungicide Laboratory only one of the chemists was provided with apparatus for the electrolytic determination of copper, so that only a few results by this method are shown. In the case of a paste, it can be weighed out directly for the determination of copper, unless the amount of moisture is particularly desired. It was found that calcium sulphate retained small amounts of copper either in an ammonical or acetic acid solution, so that the directions for the determination of copper by the thiosulphate method have been changed so as to avoid filtration, as given in the following:

(b) Dissolve 2 grams of the dry powdered sample in about 50 cc. of 10 per cent nitric acid, add ammonium hydroxid in excess and heat; then, without filtering off the precipitate which is formed, boil off excess of ammonia, add 5 to 10 cc. of acetic acid, cool, add 10 cc. of potassium iodid solution (30 grams potassium iodid to 100 cc.), and titrate with standard thiosulphate solution as described on page 241 of Bureau of Chemistry Bulletin 107, Revised.

It is recommended that the methods offered for the determination of moisture be adopted as provisional, and that the other methods be adopted as official.

BORDEAUX WITH PARIS GREEN.

The results obtained on the sample of Bordeaux-Paris green sent out are as follows:

Bordeaux with Paris green.

ANALYST	MOISTURE	CARBON DIOXID	COPPER (ELECTROLYTIC)	COPPER (THIOSULPHATE)	TOTAL ARSENIC AS As_2O_3	WATER—SOLUBLE As_2O_3
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
W. B. Ellett and H. H. Hill, Virginia	......	......	....	16.60	....	......
	......	......	....	16.50	....	......
	......	......	....	16.55	....	......
	......	......	....	16.50	....	......
Average	......	......	....	16.54	....	......
O. B. Winter, Michigan	3.37	1.98	....	15.46	19.20	4.30
	3.44	1.97	....	15.56	19.14	4.34
	......	......	....	15.66	....	......
Average	3.41	1.98	....	15.56	19.17	4.32
E. L. Griffin, Washington, D. C.	3.42	2.25	....	16.14	18.18	......
	3.39	2.28	....	16.16	18.38	......
	3.41	2.27	....	16.15	18.28	......

Bordeaux with Paris green.—Concluded.

ANALYST	MOISTURE	CARBON DIOXID	COPPER (ELECTROLYTIC)	COPPER (THIOSULPHATE)	TOTAL ARSENIC AS As_2O_3	WATER—SOLUBLE As_2O_3
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
W. J. Morgan, Washington, D. C.	......	......	16.17	......	18.81	......
	......	......	16.17	......	18.91	......
	......	......	16.21	......	......	......
Average	......	......	16.18	......	18.86	......
Geo. P. Koch, Minnesota	2.08	2.10	......	......	17.51	3.92
	2.15	2.09	......	......	17.98	3.92
	......	2.11	......	......	......	......
Average	2.12	2.10	......	......	17.75	3.92
F. L. Elliott, Washington, D. C.	......	......	......	......	18.77	......
	......	......	......	......	18.83	......
Average	......	......	......	......	18.80	......
A. K. Balls, Washington, D. C.	......	......	16.23	......	......	......
	......	......	16.16	......	......	......
	......	......	16.28	......	......	......
Average	......	......	16.22	......	......	......
E. R. Tobey, Maine	3.23	2.15	16.40	16.52	19.62	4.92
	......	......	16.48	16.39	19.82	4.92
Average	3.23	2.15	16.44	16.46	19.72	4.92
R. C. Roark, Washington, D. C.	3.38	2.23	[1]16.10	16.14	18.20	4.53
	......	2.13	[1]16.33	16.19	18.40	4.53
	......	......	......	16.21	......	4.47
Average	3.38	2.18	16.22	16.18	18.30	4.51

[1] Determined according to electrolytic method for copper in Bordeaux-lead-arsenate.

Here again the lack of suitable apparatus prevented most of the coöperators from making electrolytic determination of copper. In general, the results on moisture, carbon dioxid and copper by the thiosulphate method agree very well. Total arsenic varies more than it should.

It was found that the method given under Bordeaux-lead arsenate for the electrolytic determination of copper worked very well when applied to a Bordeaux-Paris green. It was also found that the arsenious oxid (As_2O_3) could be easily determined by the method of either Hedges or Smith, as might have been expected.

Total arsenious oxid in Bordeaux-Paris green.

ANALYST	DISTILLATION METHOD	HEDGES METHOD	SMITH METHOD
	per cent	*per cent*	*per cent*
R. C. Roark, Washington, D. C.	18.20	18.30	18.33
	18.40	18.50	18.33
	......	18.53	18.50
Average	18.30	18.44	18.39

The results on water-soluble arsenious oxid, as shown in the table on pages 448 to 449, vary from 3.92 to 4.92 per cent. This variation is undoubtedly due to differences in the temperature of digestion. A slight difference in temperature causes a marked difference in the amount of soluble arsenious oxid found. In determining soluble arsenic in an arsenical, therefore, careful attention must be given to maintaining the temperature to the proper degree during the whole period of digestion, as well as to the ratio of water to the sample.

It is recommended that the methods for copper and arsenic be changed to the following:

METHODS FOR BORDEAUX WITH PARIS GREEN.

Copper.

(a) Determine as directed under Bordeaux-lead arsenate.

(b) Weigh 2 grams of the dry powdered sample, transfer to an Erlenmeyer flask, add 25 cc. of concentrated nitric acid and heat on the steam bath to disappearance of brown fumes. Dilute somewhat with water and boil for several minutes, then add 10 cc. of bromin water and continue boiling until all bromin is expelled. Neutralize with concentrated ammonium hydroxid and add about 5 cc. in excess. Boil a minute or so and add acetic acid in excess. Cool thoroughly, add about 3 grams of potassium iodid (or 10 cc. of potassium iodid solution, 30 grams to 100 cc.), and titrate immediately with standard thiosulphate solution in the usual way. Be careful that copper remains in solution. If copper appears to precipitate, it may be redissolved by the addition of a little acetic acid and rubbing the precipitate with a stirring rod fitted with a rubber policeman. Near the end of the titration it is well to add the starch solution in successive small quantities.

Arsenious Oxid (As_2O_3).

(a) Determine by distillation with hydrochloric acid as given under Bordeaux-lead arsenate, using 0.5 gram material for the determination. (Any arsenate present will be determined by this method and reported as As_2O_3).

(b) Determine according to either Hedges or Smith method for the determination of arsenious oxid in Paris green. Before titrating be sure that all of the copper is in solution.

BORDEAUX WITH LEAD ARSENATE.

But little work was done on this mixture. The results obtained are as follows:

Analysis of Bordeaux with lead arsenate.

ANALYST	MOISTURE	CARBON DIOXID	LEAD OXID	TOTAL ARSENIC AS As_2O_3	COPPER	WATER—SOLUBLE As_2O_3
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
O. B. Winter, Michigan	51.82	0.75	....	10.24	......	0.09
	52.24	0.75	....	10.36	......	0.09
Average	52.03	0.75	....	10.30	......	0.09
E. L. Griffin, Washington, D. C.	53.25	0.80	21.84	9.53	3.66	0.08
	....	0.82	22.05	9.46	3.59	0.08
Average	53.25	0.81	21.95	9.50	3.63	0.08
Geo. P. Koch, Minnesota	49.44	0.83	....	10.64	......	0.04
	......	0.82	....	11.13	......	0.05
	....	0.87	....	......	......	0.04
Average	49.44	0.84	......	10.89	......	0.04
E. R. Tobey, Maine	......	.....	......	......	......	0.14
	......	.....	......	......	......	0.14
Average	......	.....	24.10	......	3.82	0.14
F. L. Elliott, Washington, D. C.	......	.....	......	10.23	......	......
	......	.....	......	10.23	......	......
	......	.....	......	10.17	......	......
Average	......	.....	......	10.21	......	......
A. K. Balls, Washington, D. C.	......	.....	......	......	3.68	......
	......	.....	......	......	3.70	......
Average	......	.....	......	......	3.69	......
R. C. Roark, Washington, D. C.	53.03	0.79	22.18	9.86	3.70	0.08
	......	......	......	10.06	......	0.07
Average	53.03	0.79	22.18	9.96	3.70	0.08

The above results agree fairly well considering the difficulties in analyzing such a sample and the inexperience of the analysts with the methods.

In commenting on his results on the Bordeaux-lead arsenate and Bordeaux-Paris green, O. B. Winter stated: "I would say that the methods for determining copper, arsenious and arsenic oxids and especially the method for carbon dioxid gave closely-checking results with no difficulty whatever. The results were not good for moisture in the pastes, but the difficulty may have been due to lack of thorough mixing."

Although so reported, it is doubtful if all the arsenic in a Paris green, and more especially in a Bordeaux-Paris green, is present as As'''. Nor is it always true that all the arsenic in a lead arsenate or in a Bordeaux-lead

arsenate is present as As^{v}, although it is generally so reported. It would therefore seem advisable that methods be devised for the accurate determination of As_2O_3 and As_2O_5 in the presence of each other and in the presence of one or more of the following: copper, lead, calcium and zinc.

It is recommended that a method other than an electrolytic one be devised for the determination of lead and copper in a Bordeaux-lead arsenate.

While on the subject of arsenicals, I wish to recommend for study this coming year, methods for the determination of the important constituents of zinc arsenicals, such as zinc ortho-arsenite alone and in combination with Bordeaux.

NICOTIN.

To test the methods for the determination of nicotin, three samples were sent to the coöperating chemists, namely, one powder, one concentrated solution of free nicotin, and a dilute solution of the same to which was added a little pyridin and ammonium chlorid.

The following tables are the results.

Solution No. 2 was prepared by mixing 299.8 grams of nicotin solution No. 1 with 448.7 grams of an aqueous solution of pyridin and ammonium chlorid, the pyridin amounting to 4.64 per cent by weight and the ammonium chlorid to 3.95 per cent by weight in this aqueous solution. The theoretical amount of the ingredients in nicotin solution No. 2, as sent to the coöperators, is, therefore as follows:

Pyridin	2.78 per cent by weight
Ammonium chlorid	2.37 per cent by weight
Nicotin	16.42 per cent by weight (assuming nicotin content of solution No. 1 to be 41.00 per cent).

The coöperating chemists report on the methods for nicotin as follows:

COMMENTS BY ANALYSTS.

O. B. Winter: The official method for nicotin is rather long and tedious and gave unsatisfactory results, which, I believe, were due to the extraction with ether. The silicotungstic acid method is very satisfactory in manipulation and in giving closely-agreeing duplicates. We did not succeed with the Lloyd method. I am sending a few of the results obtained by this method, not for you to report them, but to give you some idea of our work, and possibly later in the season we may be able to try it out again. Certainly the method looks good, and if it can be used, it will be a great time saver.

S. D. Averitt: Used Lloyd's reagent and washed gasoline in analyzing the two solutions by the Lloyd method. My experience as well as that of Mr. Shedd, leads us to the conclusion that the consistency of the paste is the main point in the extraction. The paste should be so stiff that it is just on the point of crumbling for the

Determination of nicotin.

SUBSTANCE AND ANALYST	KISSLING METHOD	SILICOTUNGSTIC ACID METHOD		LLOYD METHOD
		Dried at 125°	Ignited	
POWDER:	*per cent*	*per cent*	*per cent*	*per cent*
H. H. Morgan, Delaware	0.965	1.44	1.47	1.07
	0.940	1.44	1.47	0.97
	0.965	1.51	1.52	1.04
	....	1.49	1.55	....
	....	1.45	1.48	....
	....	1.46	1.46	....
Average	0.957	1.47	1.49	1.03
A. K. Anderson, Minnesota	....	....	....	1.19
	....	....	....	1.16
	....	....	....	1.17
Average	....	....	....	1.17
E. L. Griffin, Washington, D. C.	....	....	1.42	....
	....	....	1.44	....
Average	....	....	1.43	....
O. B. Winter, Michigan	1.24	1.33	1.27	1.12
	1.30	1.31	....	0.86
	....	....	....	0.86
	....	....	....	0.56
Average	1.27	1.32	1.27	[1]
M. R. Miller, California	1.19	1.39	....	....
Average	1.19	1.39	....	....
R. C. Roark, Washington, D. C.	....	1.48	1.43	....
	....	1.51	1.44	....
Average	....	1.50	1.44	....
SOLUTION NO. 1:				
H. H. Morgan	39.62	41.29	40.94	41.01
	38.96	41.12	40.98	40.84
	39.47	41.13	40.49	40.19
	....	40.72	40.28	....
	....	41.09	40.77	....
	....	41.15	40.92	....
Average	39.35	41.08	40.73	40.68
E. L. Griffin	....	40.82	....	....
	....	40.80	....	....
Average	....	40.81	....	....

[1] Results too discordant to average.

Determination of nicotin.—Continued.

SUBSTANCE AND ANALYST	KISSLING METHOD	SILICOTUNGSTIC ACID METHOD		LLOYD METHOD
		Dried at 125°	Ignited	
SOLUTION NO. 1:—Continued	*per cent*	*per cent*	*per cent*	*per cent*
O. B. Winter	41.46	41.42	41.18	37.71
	....	41.42	41.23	....
	....	....	41.14	....
	....	....	41.12	....
Average	41.46	41.42	41.17	37.71
M. R. Miller	41.60	40.96	41.11	40.10
	41.40	40.90	....	....
	....	41.02	....	....
Average	41.50	40.96	41.11	40.10
S. D. Averitt, Kentucky	....	....	....	41.17
	....	....	....	40.84
	....	....	....	40.82
Average	....	....	....	40.94
W. B. Ellett and W. G. Harris, Virginia	....	40.82	40.89	....
	....	40.89	41.19	....
	....	40.90	....	....
Average	....	40.87	41.04	....
R. C. Roark	....	40.86	40.92	40.27
	....	40.98	41.06	....
Average	....	40.92	40.99	40.27
SOLUTION NO. 2:				
H. H. Morgan	16.14	16.00	16.21	15.70
	....	16.42	15.99	15.96
	....	16.14	15.90	16.93
	....	16.32	15.97	....
	....	16.44	16.64	....
	....	16.66	16.69	....
Average	16.14	16.33	16.23	16.20
O. B. Winter	16.92	16.74	16.86	....
	....	16.86	16.76	....
Average	16.92	16.80	16.81	....
M. R. Miller	....	16.76	16.80	17.41
	....	16.72	16.75	15.18
	....	....	....	16.21
	....	....	....	15.17
Average	....	16.74	16.78	15.99

Determination of nicotin.—Concluded.

SUBSTANCE AND ANALYST	KISSLING METHOD	SILICOTUNGSTIC ACID METHOD		LLOYD METHOD
		Dried at 125°	Ignited	
	per cent	*per cent*	*per cent*	*per cent*
SOLUTION NO. 2—Continued				
S. D. Averitt	....	....	....	17.62
	....	....	....	17.59
	....	....	....	17.81
Average	....	....	....	17.67
W. B. Ellett and W. G. Harris	....	16.26	16.14	....
	....	16.36	16.70	....
	....	16.20	....	....
Average	....	16.27	16.42	....
R. C. Roark	....	16.87	16.58	....
	....	16.65	16.79	....
Average	....	16.76	16.69	....

Theoretical = 16.42.

first two or three extractions. It may then be thinned with a few drops of water. In this almost crumbly condition of the magma the extractant can be made to reach perfectly every part of the mass and five or six extractions are usually sufficient.

H. H. Morgan: In Lloyd's method for nicotin the indicator used, an aqueous extract of litmus, proved very unsatisfactory, the end point not being sharp. In the silicotungstic acid method (b) a considerable amount of the precipitate was washed through the filter (S. & S. 589 blue ribbon). Possibly this could be avoided by reducing the amount of precipitate, or by using a wash stronger in acid.

M. R. Miller: Of the methods used, the one which gave the best satisfaction was the silicotungstic acid method. The Kissling method gives trouble in the final titration using cochineal as indicator as it is found that the end point when nicotin is present in the solution is obscure and difficult to decide upon. In the Lloyd method which was submitted the preparation of the sample for titration is much more cumbersome than that of the method of Bulletin 102, of Bureau of Plant Industry, and in the final titration, there is nothing gained by the use of litmus (azolitmin in this laboratory) as an indicator, the end point in this case being even more obscure than that obtained when cochineal is used in the Kissling method. In the silicotungstic acid method, there is less chance for the personal equation to affect the results and consequently the results should be found to be more uniform when given by different workers.

The results by the silicotungstic acid check very closely, and almost all of the coöperators who tried all the methods expressed their preference for this method. It is very accurate and is preferable in many ways to the other methods. It is recommended that this method be adopted as an official one, and that the precipitate of nicotin silicotungstate be

ignited rather than dried at 125°. The ignition method is quicker, and in general, more accurate.

The referee cannot see any advantage in the Lloyd method for the determination of nicotin as regards quickness, and it certainly is not to be compared in accuracy with the silicotungstate method. It is recommended, therefore, that no further work be done on it.

It should be said that the directions for the Lloyd method as sent out by the referee aimed to overcome the difficulties encountered in using this method as published in Bureau of Chemistry Bulletin 56, pages 114 to 115, which was tried out by the association in 1898 and again in 1902 (Bur. Chem. Bul. 81, p. 203), and found to be inaccurate. Although the modifications introduced seem to have improved the method, still it is far from being satisfactory and in view of the greater accuracy and adaptability of the silicotungstate method the necessity for the Lloyd method is not apparent.

RECOMMENDATIONS.

It is recommended—

(1) That Method I for total arsenious oxid in Paris green, as described on pages 25 to 26, Bureau of Chemistry Bulletin 107, Revised, be changed as described in Method I, page 445 of this report.

(2) That Methods II and III for total arsenious oxid in Paris green (Bur. Chem. Bul. 107, Rev., pp. 26–27) be discarded.

(3) That Methods II and III for total arsenic in Paris green, pages 445 to 446 of this report, be adopted as official.

(4) That the method for the determination of moisture in Bordeaux mixture, as described on pages 436 to 437 of this report, be adopted as provisional.

(5) That the method for the determination of carbon dioxid in Bordeaux mixture, as described on page 437 of this report, be adopted as official.

(6) That the electrolytic method for the determination of copper in Bordeaux mixture, as described on page 437 of this report, be adopted as official.

(7) That the thiosulphate titration method for the determination of copper in Bordeaux mixture, as described on page 448 of this report, be adopted as an optional official method.

(8) That the method for moisture in Bordeaux-Paris green, as described on page 437 of this report, be adopted as provisional.

(9) That the method for carbon dioxid in Bordeaux-Paris green, as described on page 437 of this report, be adopted as official.

(10) That the method for water-soluble arsenious oxid in Bordeaux-Paris green, as described on page 438 of this report, be adopted as provisional.

(11) That the distillation method for the determination of total arsenic in Bordeaux-Paris green, as described on page 438 of this report, be adopted as official.

(12) That the methods of C. M. Smith and C. C. Hedges for the determination of total arsenious oxid in Paris green, as described on page 446 of this report, be made optional official methods for the determination of total arsenious oxid in Bordeaux-Paris green.

(13) That the electrolytic method for the determination of copper in Bordeaux-lead-arsenate, as described on page 438 of this report, be made an official method for the determination of copper in Bordeaux-Paris green.

(14) That the thiosulphate titration method for the determination of copper in Bordeaux-Paris green, as described on page 450 of this report, be made an optional official method.

(15) That the method for moisture in Bordeaux-lead arsenate, as described on page 438 of this report, be adopted as provisional.

(16) That the method for the determination of carbon dioxid in Bordeaux-lead arsenate, as described on page 438 of this report, be adopted as official.

(17) That the method for water-soluble arsenic oxid in Bordeaux-lead arsenate, as described on pages 438 to 439 of this report, be adopted as provisional.

(18) That the electrolytic method for the determination of copper in Bordeaux-lead arsenate, as described on page 438 of this report, be adopted as official.

(19) That the method for the determination of lead oxid in Bordeaux-lead arsenate, described on page 438 of this report, be adopted as official.

(20) That procedure (b) of the silicotungstate method for the determination of nicotin, as described on page 439 of this report, be adopted as official.

(21) That no further work be done on the Lloyd method for the determination of nicotin.

(22) That the coöperative work on insecticides for next year comprise a study of the following:

(a) Methods for the determination of $As^{\cdots}$ and As^{v} in the presence of each other and in the presence of one or more of the following: lead, copper, zinc, and calcium.

(b) A method other than an electrolytic one for the determination of copper, lead and arsenic in a Bordeaux-lead arsenate mixture.

(c) Methods for the determination of the principal ingredients in zinc-arsenic compounds alone and in combination with Bordeaux mixture.

The honorary president, H. W. Wiley, made a short address to the association, touching upon the effects of the war in Europe on science and agriculture in this country, especially on the supply of potash needed for our soils.

REPORT ON WATER.

By W. W. Skinner (Bureau of Chemistry, Washington, D. C.), *Referee.*

The results of the coöperative work on the determination of strontium which were reported in 1912 and 1913 were so unsatisfactory, the results being uniformly low, that the referee for last year suggested that a critical study of the method be made. In view of the results obtained it was decided to be inadvisable, therefore, to undertake further coöperative work until some conclusion could be reached as to the cause or causes for the low results. The method which has been used in the coöperative work heretofore for the separation and determination of calcium and strontium is that of Stromeyer-Rose as modified by Hillebrand. Briefly, it is the precipitation of strontium and calcium as oxalates, washing with cold water, igniting and weighing the mixed oxids, converting the oxids into nitrates, digestion of the nitrates with an ether alcohol mixture, filtering off the solvent containing the calcium nitrate, converting the strontium into sulphate and weighing. The calcium being obtained by difference by subtracting the calculated weight of strontium oxid from the weight of the mixed oxids.

While the results for strontium which have been reported by this method have been uniformly low the calcium which has been obtained by difference has generally agreed very well with theory, indicating that the loss in strontium is probably due entirely to the solubility of the oxalate. The solubility of calcium oxalate which has been pretty fully determined by Holleman, Kohlrausch, and others and later by Richards, McCaffry and Bisbee, is slight, being of the order of 0.4 mg. of calcium in 200 cc. of cold water, the maximum amount of wash ordinarily used in analysis, and 0.9 mg. in water at 95°C. This solubility is sufficiently small to be of no very great significance in ordinary analytical work. The same, however, is not true of strontium oxalate which according to Kohlrausch is soluble in water at 18° to the extent of 4.6 mg. per 200 cc. expressed as strontium and to the extent of 6.6 mg. per 200 cc. at ordinary temperature, as reported by Treadwell.

In order to understand better the significance of the effect of the solubility of strontium oxalate it was thought advisable to check these results under actual working conditions as the method is ordinarily employed and also to test the effect of various wash solutions with the object of reducing the solubility to the lowest possible point. Solutions of calcium and strontium salts were prepared and very carefully standardized. For purposes of comparison it was thought advisable to treat calcium oxalate with the same wash solutions which it was proposed to use for strontium oxalate. In each series the following wash solutions were used: 200 cc. of cold water; 200 cc. of hot water; 200 cc. of water charged with carbon

dioxid; 200 cc. of 1 per cent ammonium oxalate solution; 200 cc. of 1 per cent ammonium hydroxid solution.

Since some distilled water contains considerable carbon dioxid it was suggested that it might influence the solubility of the oxalates, hence the reason for using this wash. The maximum solubility of calcium oxalate in any of these solutions was 1.2 mg. calcium when hot water was used, which is probably high since the average of four determinations was only 0.5 mg. per 200 cc. Even this slight solubility was materially reduced, however, when a 1 per cent ammonium oxalate solution was substituted for hot water in the washing of the oxalate precipitate, the maximum solubility being 0.1 mg. per 200 cc. while in two of the four experiments the result was zero.

The precipitated strontium oxalate was washed in the same manner using the five solutions named above. The greatest solubility was noted for hot water, the maximum being 10.4 mg. of strontium per 200 cc. of wash water. A maximum of 8.3 mg. was obtained when cold water was used as prescribed in the method which shows that the solubility of strontium oxalate is of such an order as to cause very serious discrepancies in the results obtained by the method when used for the separation of relatively small amounts of strontium from large amounts of calcium. The solubility of strontium oxalate in a wash of 1 per cent ammonium oxalate solution was found to be very much less than it is when cold water is used, the maximum being 2.1 mg. with an average of 1.1 mg. The solvent effect of the 1 per cent ammonium hydroxid solution seemed to be quite as great as cold water. These preliminary results indicate that the substitution of a 1 per cent ammonium oxalate solution for washing the mixed oxalates would add very materially to the accuracy of the method by reducing the loss due to the solubility of strontium oxalate as well as exert a favorable influence on the determination of calcium.

For the purpose of checking the determination of calcium the method suggests the advisability of determining calcium in the ether alcohol mixture used for the separation of the calcium and strontium nitrates. It has been found, however, that the results by this "direct" method are invariably low and this is true even when the results by the "indirect" method give figures for calcium which are in practical agreement with theory. It was thought that possibly the small amount of solvent prescribed in the method for digesting the dried nitrates, namely, 3 to 5 cc. of ether alcohol mixture, was not sufficient to remove all of the calcium nitrate. A number of experiments were therefore run using various amounts of ether alcohol mixture from 5 to 40 cc. The loss expressed in terms of calcium varied from 1.6 mg. when 5 cc. of solvent were used to 2.3 mg. when 40 cc. were used, indicating that the quantity of solvent used in digestion was not the factor upon which the error depends. It seems

Solubility of calcium oxalate under working conditions.

Used for washing	200 cc. of cold water	4 determinations	0.0 to 0.3 mg.
	200 cc. of hot water	4 determinations	0.0 to 1.2 mg.
	200 cc. of carbonated water	4 determinations	0.0 to 0.2 mg.
	200 cc. of 1 per cent ammonium oxalate solution	4 determinations	0.0 to 0.1 mg.
	200 cc. of 1 per cent ammonia solution	4 determinations	0.07 to 0.3 mg.

Solubility of strontium oxalate under working conditions.

Used for washing	200 cc. of cold water	6 determinations	4.6 to 8.3 mg.
	200 cc. of hot water	7 determinations	8.1 to 10.4 mg.
	200 cc. of carbonated water	2 determinations	6.3 and 6.9 mg.
	200 cc. of 1 per cent ammonium oxalate solution	4 determinations	0.2 to 2.1 mg.
	200 cc. of 1 per cent ammonia solution	2 determinations	4.4 and 4.6 mg.

Showing calcium remaining with the strontium after treatment with ether alcohol mixture using varying amounts of solvent and subsequent washing.

With	5 cc. of solvent; 3 determinations error as calcium		1.6 to 1.8 mg.
	10 cc. of solvent; 3 determinations error as calcium		1.9 to 2.1 mg.
	15 cc. of solvent; 1 determination error as calcium		1.7 mg.
	20 cc. of solvent; 3 determinations error as calcium		1.7 to 2.3 mg.
	30 cc. of solvent; 1 determination error as calcium		1.2 mg.
	40 cc. of solvent; 1 determination error as calcium		2.3 mg.

evident, however, from the results that a single extraction with ether alcohol is not sufficient where a high degree of accuracy is desired but that it is necessary after washing to redissolve in water the dried precipitate of strontium nitrate, contaminated with small amounts of calcium nitrate, evaporate to dryness, and extract again with the ether alcohol solution.

As a result of this preliminary work it is suggested that the method for the separation and determination of calcium and strontium be modified by substituting a solution of ammonium oxalate for the cold water prescribed in the present method for washing the mixed oxalates and that at least two extractions of the mixed nitrates with the ether alcohol solvent be made, instead of one as prescribed in the present method.

The matter is referred to the referee for next year for further study.

REPORT OF COMMITTEE ON AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

By C. B. Williams (Agricultural Experiment Station, Raleigh, N. C.), *Chairman.*

Since the last meeting of the association, the committee has held one meeting at which the different phases of the work now in progress were thoroughly discussed.

The inauguration of the work, of necessity, has been slow chiefly because of the difficulty in getting the soil, selected for the investigations, thoroughly exhausted of phosphoric acid, and to a less extent in finding the land, selected for the field work, to show a lack of uniformity during the preliminary stages of the work to such an extent that in some cases new fields had to be selected for carrying on the investigations. It is thought best by the committee, in consideration of these facts, to reserve the data which it now has in hand from some of those coöperating in the investigations, to present later with such recommendations as seem justified by the results, when more results and fuller reports have been received.

There are coöperating in the field experiments seven station workers and in the pot culture investigations eleven workers. The committee has up to this time received four preliminary field reports and seven reports from those coöperating in the pot culture experiments.

During the coming year, the committee expects to prosecute the work aggressively and hopes to make a final report as soon as all the experiments have been completed.

William Frear, chairman of the Committee on Food Standards, reported that since there had been appointed a committee to coöperate with other

committees on food definitions it seemed practical to drop the old committee on food standards. A motion that this committee be discharged was carried by the association.

REPORT OF COMMITTEE TO COÖPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS.

By William Frear (Agricultural Experiment Station, State College, Pa.), *Chairman.*

An advisory committee composed of one member from each committee of three has held meetings and assigned to each member of the joint committee subjects for study, as evaporated milk, asafetida, cereal preparations, and iodin solutions. Grade standards have been considered but as yet no action has been taken. Certain difficulties are commonly urged against minimum standards which a well-devised system of grade standards would remedy; the responsibilities and the monetary values involved are great. All sides of each question must be considered as decisions should not be too theoretical or unfair to manufacturers where slight changes might lead to greater expenditures than are for the good of the public. The committee is down to careful work and good coöperation and is establishing fundamental facts.

No report was made by the chairman of the Committee on Editing Methods of Analysis.

REPORT OF COMMITTEE ON THE STUDY OF VEGETABLE PROTEINS.

By Thomas B. Osborne (Agricultural Experiment Station, New Haven, Conn.), *Chairman.*

When my appointment as chairman of the Special Committee on Study of the Vegetable Proteins was announced to me by the secretary he told me that it was the idea of the association that I should plan the work and have it done by others. I was also to appoint two other members of the committee.

As Mr. Alsberg and I had already discussed many of the problems involved in a comprehensive study of the vegetable proteins I asked him to join me on this committee and to arrange for further consideration of the work to be done. As it was manifestly impracticable to undertake any laboratory work on this subject during the present year it was not thought necessary to appoint a third member. It was agreed that work in this difficult field of research should not be begun until some means

could be found whereby it could be conducted under conditions that would assure its continuation for a sufficient time to enable those engaged in the work to acquire skill and experience in the methods of isolating and separating the proteins from one another, and in the various methods employed in studying their properties. When such experience has been gained it is believed that a large number of the commercially important seeds should be carefully investigated as of the proteins of many of these we have at present no knowledge whatever. These studies should be further extended to the proteins of other parts of plants which are used as food, and of which, as yet, there is no information available.

The importance of such knowledge is becoming every day more evident since the study of the relative nutritive value of the few proteins which are available for comparison is revealing wide differences in their nutritive value. We can no longer be content to estimate the food value of vegetable products by simply determining their content of protein nitrogen since the relative proportion of the amino-acids which these yield determines to a very large extent their value in nutrition.

Future progress in the study of many important problems in animal, as well as human, nutrition demands that our knowledge of the individual proteins in the different materials used for food be greatly extended. To do this will require a great deal of patient and laborious work, which can be done only by those trained in this special field. There are very few men in this, or any other, country who have had experience in extracting, purifying and studying vegetable proteins, and it will be necessary to train from the beginning most of those who are to take part in such studies. To properly and effectively conduct such work will cost more than most experiment stations will probably be willing, or able, to devote to it. It has seemed to us, therefore, a subject which the Bureau of Chemistry was best able to take up, and a very suitable line of research for it to follow.

Mr. Alsberg and I have agreed to coöperate in attempting to organize work along these lines, but are not willing to begin until the right men can be secured to undertake it. This has been found difficult, and as a consequence we cannot now report any definite plans that are being actually put in operation. We hope, however, that our efforts will sooner or later meet with success and that before long an extensive study of the vegetable proteins will be begun.

In view of the peculiar difficulties presented by an effective study of the vegetable proteins we do not consider that this subject is one that can be dealt with successfully by coöperative work by the association. We recommend that the special committee appointed to report on the study of the vegetable proteins be discontinued, but that all the members of the association give their support to work in this field whenever suitable means are found for properly undertaking it.

C. L. Alsberg gave a short supplementary talk, on the need of the isolation and hydrolysis of proteins present in seeds and of laying a foundation for feeding and nutrition work. He stated that since it seemed best for this work to be carried on in the Bureau of Chemistry, the subject has been taken up with the Secretary of Agriculture and a small item under biological investigations inserted in the appropriation. The work is being organized in the Bureau and it is hoped that a number of papers on vegetable proteins may be ready for the next meeting.

An invitation was extended by C. B. Lipman to the association to hold the 1915 meeting in San Francisco or Berkeley. After the president read the list of cities and organizations sending invitations, the motion that the association meet in 1915 in San Francisco or general vicinity at a date agreeable to other scientific associations, was carried. On the afternoon of the following day, R. N. Brackett made the resolution which was seconded by E. W. Magruder that the next place of meeting be reconsidered and made a new motion that the meeting be held in Washington. After discussion by B. B. Ross and H. C. Lythgoe showing how much more work is accomplished when the meetings are held in Washington, the new motion for Washington as the next meeting place was carried.

No report was made by the chairman of the Committee of Review of the Analysis of Lime Sulphur Solutions.

The meeting adjourned at 4.30 p.m. for the day.

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON FOOD ADULTERATION.

By Julius Hortvet (State Dairy and Food Department, St. Paul, Minn.), *Referee*.

The work of the present season has been characterized by the completion or rounding out of several lines of investigation which have been under way during the past two years. An unusual number of the associate referees have brought their work to such a satisfactory state that definite recommendations may be made for final adoption of methods or for further study along well-defined lines. The reports submitted tend in the main to indicate a continued interest in the work and purposes of this association; there have been prompt and fairly complete returns from the collaborators and adequate outlines or full reports from the associate referees in ample time for consideration before the date of this meeting. Details of the results accomplished will be fully presented as the referees' reports are read, but it may be appropriate to refer briefly to a few salient features of these reports.

An important advance has been made in the development of the uranyl acetate and ammonium molybdate polarization methods for determining malic and tartaric acids in fruit juices, jellies, sirups, and other fruit products. In the case of malic acid the associate referee proposes a general method applicable to fruit products and other substances, and also recommends the further study of a modified method for citric acid which involves a new principle discovered by L. W. Andrews. Working on this principle, it is promised that a very simple procedure can be developed for the estimation of citric acid.

The referee on flavoring extracts has confined the work of the present year to a comparative study of various methods for determining essential oil in extracts of anise, cassia, cinnamon, clove, nutmeg, peppermint, spearmint and wintergreen. The relative merits of the various methods which have been proposed in recent years are quite adequately shown up on the part of half a dozen experienced collaborators. The chief difficulties attending the analysis of such extracts as peppermint, clove and nutmeg, it is believed, have been finally overcome, and the associate referee is able to make definite recommendations to the association, which,

if favorably considered, will add several new methods which are now recognized as having established value.

An examination of the reports received on heavy metals reveals important progress toward the perfection of methods for the accurate determination of such heavy metals as lead, arsenic, and tin. The so-called modified Gutzeit Method for arsenic has been carefully tried out under various conditions and three important methods for estimating tin have been subjected to critical study. The work on lead has been carried out by the associate referee on baking powder and baking powder materials. No collaborators have assisted in this work during the past year, but the associate referee reports that he has now perfected the modified procedure of Seeker and Clayton in such form as to be prepared to subject the method to a careful collaborative study with a view to final adoption at the next meeting. It is also definitely proposed that methods for copper, zinc, nickel and aluminum be made new subjects for study during the coming year.

The work of the associate referee on colors has been devoted chiefly to the study of the separation and identification of the coloring matters naturally occurring in fruits. The outline of the work submitted indicates a large amount of original painstaking investigation, and the report on colors is an excellent illustration of the importance of assigning subjects to specialists in various lines and of the great necessity that one man be allowed ample time in which to develop and complete his investigation of the subject under his charge. When the scheme proposed by the associate referee on colors has been perfected and is available for general laboratory use, our equipment for routine examinations of foods and other products will be greatly increased.

The associate referee on saccharine products has taken up a line of investigation which when completed will serve a good purpose. The work of this season has consisted of a study of nine methods for the detection of artificial invert sugar in honey. Samples were submitted to eight collaborators and results which have been received very materially aid us in arriving at a conclusion respecting the relative merits of the different methods, some of which are virtually modifications of the original Fiehe's test. Some of these tests will be eliminated as a result of the work of the present year, and it remains to be seen which of the nine methods now under consideration will survive after an additional year's careful examination.

In connection with the work on wine it may be confidently stated that the associate referee has succeeded in bringing details of the method proposed by Hartmann and Eoff to such a stage that it will be possible to consider favorably its adoption at the present meeting. By means of two important modifications, one of which consists in an important change in

the manner of using the indicator during titration, the method is brought into such a form that analysts may place increased reliance upon the results obtained for tartaric acid.

The work of the associate referee on preservatives has followed out the recommendations approved by the association at its last meeting, and has been confined to the collection of further data concerning the occurrence of formic acid or what appears to be this substance in natural products, and to a study of the influence of possible interfering substances upon the Fincke determination and the relative value of qualitative tests. This work has been conducted without the assistance of collaborators, but the referee has gone into the subject to such a thorough extent that the association will be presented with results which may be regarded as amply establishing the limits of formic acid naturally occurring in various kinds of products. It is believed that the work of the collaborators of last year upon the Fincke method justifies recommending this method for provisional adoption. The referee is not prepared to recommend a qualitative test which can be considered reliable in the hands of inexperienced analysts, and recommends that the association take up a study of quantitative methods for estimating saccharin.

The work on oils and fats has been devoted to the study of two important methods for detection of phytosterol in mixed animal and vegetable fats. This is a subject which has not heretofore been under investigation by this association, and it is satisfactory to note not only that it has been deemed advisable to undertake this work, but also that the report of the associate referee reaches conclusions which are of value. Of the two methods which have been subjected to comparison, it may be stated that no choice has developed between the two as respects accuracy, correct conclusions being reached by all collaborators, but that the so-called digitonin method while having advantage of simplicity and convenience, has the disadvantage of requiring an expensive reagent which is not easily obtained. The present Bureau of Animal Industry method, while requiring more time and labor, has been found to be decidedly superior to our present official method. Both methods are recommended for adoption as provisional.

The report of the referee on inorganic phosphorus in vegetable and animal tissues is a valuable contribution to the program of this meeting. The work has been carried out entirely in the laboratory of the associate referee, but results are nevertheless ample and conclusive, perhaps in many respects more satisfactory than could possibly be obtained by a number of collaborators working separately. As regards the results obtained on animal substances, conclusions point favorably to the adoption of the magnesia mixture method of Forbes and associates for determination of water-soluble inorganic phosphorus. This portion of the work is in

very satisfactory shape and appears to bring to a conclusion the very careful work which has been carried out during the past three or more years on this subject. While it is recommended that a method be adopted for animal substances, the referee has come to the conclusion that the work on inorganic phosphorus in vegetable substances be dropped.

The referee on dairy products has carried out the recommendations of this association in respect to the study of the method, with modifications, which was proposed for final adoption at this meeting. A dozen collaborators assisted in the work, and results seem to be ample in so far as they reveal the fact that we are confronted with certain difficulties which have not heretofore been fully realized. Of the three samples submitted to the collaborators, two were condensed milk products, sweetened and unsweetened, and it is chiefly in connection with results on these two kinds of products that the trouble has been disclosed. Comparative tests were carried out by the official Roese-Gottlieb method, and the results by this method are equally disappointing and tend to further magnify the importance of a special study of methods for determining fat in evaporated milk. Conversation and correspondence with chemists and manufacturers has increased the realization that we are in urgent need of a thorough investigation on this subject. Results reported at the meeting of 1913 on samples of milk, cream and ice cream were fairly satisfactory and pointed favorably toward a conclusion of the work during the past season. Assuming that reliable uniform samples were submitted to the collaborators, and we have every reason to rely on that assumption, it is impossible to conclude otherwise than that there are peculiar difficulties attending the accurate determination of fat in evaporated and condensed milk. Certain processes incident to manufacture, added to which is the recent introduction of the homogenizer by a large number of manufacturers, doubtless cause important changes in the constitution of these products to such an extent that there are unusual difficulties in separating the fat from the other ingredients by any of the methods with which we are now acquainted. It is, therefore, recommended that this subject be given special study during the coming year.

Satisfactory as the work of the past season has turned out to be, we have been nevertheless hampered by an unfortunate state of affairs respecting the publication of our proceedings. This condition has existed or has been in existence more or less seriously for a number of years. You will recall that the published proceedings of the 1912 meeting were not in evidence until the opening day of our session a year ago, and as I am writing this there is much doubt whether we are to see anything at all of the proceedings of the meeting of 1913. Respecting this last supposition, however, it matters little in so far as it affects the real situation; whether we are to be favored with a copy of our last year's proceedings or not, the

general unsatisfactory conditions still confront us—we are not kept adequately in touch with our work from year to year, there is a consequent lag in our interest, and this unbusinesslike state of affairs can but reflect unfavorably on this association as a progressive organization. It is safe to venture the prediction that the members of this association would be well pleased with at least one publication annually, and in the main, all would be well satisfied if such a publication of proceedings could be depended on to make its appearance within six months after the convention. The work of this association is important; all chemists who have in the past twenty years been in close touch with the State and Federal work in its various branches need no assurances on that point; in fact, all will insist that our work is essential, not only in the interest of the public welfare, but also in the interest of ourselves professionally. No association has worked more disinterestedly for the promotion of things purely scientific or with greater zeal and self-sacrifice for the cause of pure products and high standards of quality. We are, as a matter of fact, vitally a part of the official work of every State in the Union, and constitute an essential factor in more than one department of the Federal service. Every State chemical laboratory, whatever its departmental connection, has a vital interest in the development from year to year of the studies being carried on and the results reported by this association. With these facts in mind, may we not readily see a solution of the problem before us? It may or may not be a legal obligation on the part of any of the States or of any Federal bureau or department to make good the deficiencies which hamper our work, but all interests involved can doubtless be assembled in such shape as to formulate a plan whereby we can all rest assured of the continuance of our association as an official or at least in a serious sense, a quasi-official organization, and thereby provide also the necessary means to insure the regular and prompt appearance of our printed proceedings. It is the urgent wish of your referee that this subject be taken up at this meeting with a view to an early practical arrangement whereby we may rest assured in the future regarding the proper care of such publications as are deemed essential to our work.

Furthermore, year by year our work has before it a definite purpose; we naturally like to see our results from time to time brought into definite form, stripped of nonessentials, and brought down to date. We have on our hands a mass of old matter that it would seem pleasant to discard, methods that are obsolete, data that should be revised or entirely thrown out. Bulletin 107, Revised, is now old; there are six years since its publication, probably seven or eight years since its compilation; and this constitutes a long period of time as we are in the habit of measuring time in terms of chemical events. All of us, whether beginners, independent

investigators, or more or less confirmed followers of routine, habitually refer to the Official and Provisional Methods of Analysis; in a sense it is not only our duty as official chemists but it is also often a legal necessity. We have thumbed the leaves of Bulletin 107 so often that its pages have begun to stale, yet we hold no sacred views respecting a document that is so old as to be in many features out of date or at worst a relic of earlier ideals and habits of thought. We are now in a mood to demand a revision of 107, Revised—better, in fact, to require a complete new compilation which shall embody not only all that is good and permanent in the publication now in print, but also all that has been well tried out and finally adopted by the association during the past six years. It is hoped that such revision or rather compilation is now well under way; and that a new bulletin of official methods of analysis will be in our hands at an early date. Therefore, as a second recommendation, I would urge that this association consider the question as to progress now being made on a compilation to date of our official provisional methods of analysis to supersede Bulletin 107, Revised, and that we arrange at this meeting a definite plan whereby the work may be carried out to completion at an early date, and whereby the expense of publication may be satisfactorily met.

REPORT ON COLORS.

By W. E. Mathewson (Bureau of Chemistry Food and Drug Inspection Laboratory, New York, N. Y.), *Associate Referee.*

The coöperative work on colors for the past three or four years has been confined chiefly to the coal tar dyes. These being of well understood chemical nature the analysts have had at their disposal much reliable information concerning the properties of the individual substances and one of the main problems has been the selection of the characteristics best suited for practical analytical work. By the use of immiscible solvents, supplemented in a few cases by chemical methods, it would seem that most dye mixtures likely to be met may be separated satisfactorily and their identification completed by well-investigated reactions.

This year it was hoped that similar methods might be extended to the commonly-occurring natural coloring matters. These present more difficulty because of the limited solubility in organic solvents of many of them, their frequent occurrence in admixture with one another and especially because of the lack of much exact knowledge concerning them. After some experimental work by the associate referee, however, it seemed that little would be gained by sending out samples for analytical investigation by methods now in use whose limitations are already known, and a circular letter was sent to the collaborators stating this and expressing

the hope that any new data might be published or be communicated to the other analysts through the associate referee as soon as possible.

The experimental work just mentioned failed to bring out distinctions sufficiently marked to be of use in analysis between the coloring matters of a number of common fruits, authentic samples of the juices of cherries, blackberries, raspberries, currants, grapes and huckleberries having been kindly furnished for this work by H. C. Gore of the Bureau of Chemistry. These coloring matters, though extracted in relatively small amount by amyl alcohol from acid solutions, were found to be rather readily changed by heating with dilute hydrochloric acid, substances similar in color reactions but much more soluble in amyl alcohol being formed. These derived colors were obtained fairly free from other substances by treatment of the fruit juice with excess of neutral lead acetate solution (practically all coloring matter was thrown down), washing the precipitate with water several times by centrifuge until sugar, etc., were removed, solution of the coloring matter by treatment of the precipitate with 10 per cent hydrochloric acid, and extraction of this solution with amyl alcohol to remove substances directly taken up by this solvent.

The hydrochloric acid solution was then boiled a few minutes and finally again shaken out with amyl alcohol. The new coloring matter formed by hydrolysis of the glucosid was then extracted in large proportion and the amyl alcohol solution was freed from hydrochloric acid, lead chlorid, etc., by washing four or five times with water.

This plan of separation offered the advantage that it could be incorporated with work already done, giving a qualitative method for separating these colors from all those not changed in solubility by warming with acids (especially the coal tar dyes). The coloring matters obtained, however, were very similar or identical in their behavior toward reagents tried. The red amyl alcohol solutions when shaken with caustic soda solution in absence of air gave up the color to the aqueous layer in all cases forming deep green solutions almost instantly becoming brown in the presence of oxygen. The spectra of the red solutions showed a diffuse absorption band in the greenish yellow, those of the green solutions a much more sharply-defined band in the orange red.

Recently R. Willstaetter[1] has carefully investigated the coloring matters of a number of common fruits and flavors. In general he has found them to consist of glucosids (anthocyans) that on warming with acids break down into new coloring matters (anthocyanidins) and sugar, etc. The anthocyanidins form blue phenolic salts with alkalies, red oxonium salts with acids. The facts brought out in this research will be of great value in the development of analytical methods.

[1] Sitzungberichte der Königlich Preussichen Academie der Wissenschaften, 1914, p. 402.

Bearing on the analysis of coal tar dye mixtures, work by Kehrmann, Havas and Grandmougin[1] has indicated that a number of common basic dyes containing completely alkylated amino groups (for example, methyl violet, methylene blue) suffer rearrangement from the ortho-quinoid to the para-quinoid form on treatment with alkali, this being accompanied by a splitting off of an alkyl group. When such dyes, therefore, are separated from mixtures by shaking out their alkaline solutions with ether, etc., the original coloring matter may not be obtained on treatment with acid, but a lower alkylated derivative.

Gowing-Scopes[2] has recently studied the solubilities of a large number of coal tar dyes in the newer chlorhydrocarbons that have become of technical importance. Tetrachlor- and pentachlorethane and di-, tri-, and tetrachlorethylene were investigated in their relation to 45 dyes (as well as a large number of other substances) and separations based on extraction of the dry coloring matters are indicated. The dyes are described by trade names which in some cases are rather indefinite.

It is recommended that the investigation of methods for the separation and identification of the important natural coloring matters be continued by the association.

REPORT ON SACCHARINE PRODUCTS.

By F. L. Shannon (State Analyst, Lansing, Mich.), *Associate Referee.*

Detection of Artificial Invert Sugar in Honey.

The work during the last year consisted of a study of the methods for the detection of artificial invert sugar in honey. A review of the literature revealed the fact that numerous tests have been proposed for this purpose, some of which are modifications of old tests while others are distinct tests in themselves. They are all color reactions and depend upon the presence of furfural or furfural derivatives. In the past, various workers have commented on the reliability of various tests. It seems that there are more or less confusion and contradictory statements in regard to the different tests, some claiming that one test is perfectly reliable for the detection of artificial invert sugar in honey, while others claim that the same test is unreliable, the consensus of opinion, however, being that there is no single test that can be depended upon unless supplemented by further work.

It was, therefore, attempted in this work to select only those tests which had met with the greatest success in the hands of others. Nine of the most common tests were selected and instructions sent out to the collaborators along with the samples.

[1] Ber. d. chem. Ges., 1913, **46**: 2131, 2802; 1914, **47**: 1881.
[2] Analyst, 1914, **39**: 4.

PREPARATION OF SAMPLES.

Six samples were prepared as follows:

Sample A: Pure honey.

Sample B: Pure honey + 5 per cent commercial invert sugar.

Sample C: Pure honey + 20 per cent commercial invert sugar.

Sample D: Pure honey + 50 per cent commercial invert sugar.

Sample E: Pure honey + 5 per cent Herzfeld sirup.

Sample F: Pure honey + 20 per cent Herzfeld sirup.

The commercial invert sugar was obtained on the open market.

The Herzfeld sirup was prepared in this laboratory following the method of Herzfeld:[1] "One kilogram of refined sugar is heated with 300 cc. water and 1.1 gram of tartaric acid to boiling and maintained at this temperature until the solution acquires a golden yellow color (one-half to three-quarters of an hour).

COLLABORATORS.

The following seven collaborators who took up this work, sent in reports: Julius Hortvet (Guy A. Parkin, analyst), St. Paul, Minn.; C. E. Warriner, Fort William, Ont.; Miss N. A. Childs, Lansing, Mich.; W. C. Geagley, Lansing, Mich.; W. S. Hubbard, Ann Arbor, Mich.; N. B. Lawrence, Ann Arbor, Mich.; F. L. Shannon, Lansing, Mich.

INSTRUCTIONS TO COLLABORATORS.

To each sample submitted apply the following tests:

1. FIEHE'S ORIGINAL TEST (Analyst 1908, **33**: 397).

Reagent.—Dissolve 1 gram of resorcinol in 100 cc. of hydrochloric acid (1.19). Redistilled ether.

Manipulation.—One gram of honey is rubbed down in a mortar with ether. Filter off ether and evaporate. Moisten the residue with one drop of the reagent.

Results.—In the presence of artificial invert sugar an orange red color is developed, changing to cherry red and then to brown red. Pure honeys sometimes give a pink coloration. Note color after standing 10 minutes and again after standing 24 hours.

2. REINHARDT'S MODIFICATION OF FIEHE'S TEST (Analyst, 1910, **35**: 434).

Reagent.—Use 25 per cent hydrochloric acid instead of 38 per cent as in 1.

Manipulation.—Same as in 1.

Results.—Same as in 1.

3. HALPHEN'S MODIFICATION OF FIEHE'S TEST (Chem. Abst. 1911, **5**: 2124).

Reagent.—0.02 gram of resorcinol dissolved in a mixture of 2 cc. of dehyrated ether, 25 cc. of absolute alcohol and 3 cc. of hydrochloric acid.

Manipulation.—Same as in 1.

Results.—Halphen says that his reagent does not give a carmine color with as many flavors as the orignal Fiehe reagent.

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[1] Bur. Chem. Bul. 110, p. 64.

4. HARTMAN'S MODIFICATION OF FIEHE'S TEST (Chem. Abst., 1912, **6**: 1787).

Reagent.—Same as in 1.

Manipulation.—Add 2 drops of the reagent directly in 1 gram of the honey in a porcelain dish.

Results.—If artificial invert sugar is present a cherry red color appears the same as in the original test. Natural honeys give the reaction after standing about 45 minutes.

5. BRYAN'S MODIFICATION OF FIEHE'S TEST (Bur. Chem. Bul. 154, p. 15).

Reagent.—Same as in 1.

Manipulation.—Place 10 cc. of a 50 per cent honey solution in a test tube and run in 5 cc. of ether on top. Shake contents vigorously and allow to stand for some time until ether layer is perfectly clear; transfer 2 cc. of this clear ether solution to a small test tube, and add a large-sized drop of the resorcin solution. Shake and note the color immediately.

Results.—In the presence of artificial invert sugar the drop of acid in the bottom assumes immediately an orange-red color, turning to a dark red.

6. BROWN'S ANILIN ACETATE TEST (Bur. Chem. Bul. 110, p. 68).

Reagent.—(freshly prepared). To 5 cc. of c.p. anilin add 5 cc. of water. Add sufficient glacial acetic acid (2 cc.) to clear the emulsion.

Manipulation.—To 5 cc. of a concentrated solution of honey (1 : 1) in a test tube add 1 to 2 cc. of the anilin reagent. Allow the latter to flow down the walls of the test tube to form a layer.

Results.—In the presence of artificial invert sugar a red ring forms at the junction of the two liquids.

7. FEDER'S ANILIN CHLORID TEST (Analyst, 1911, **36**: 586).

Reagent.—(freshly prepared). To 100 cc. of c.p. anilin add 30 cc. of 25 per cent hydrochloric acid.

Manipulation.—5 grams of the honey are mixed directly in a porcelain dish with 2.5 cc. of the anilin reagent.

Results.—Bright red color indicates artificial invert sugar present. The intensity of the color is proportional to the amount present.

8. BENZIDIN ACETATE TEST (Analyst, 1913, **38**: 20).

Reagent.—Dissolve pure benzidin in dilute acetic acid to a saturated solution.

Manipulation.—2 grams of the honey are dissolved in 10 cc. of water and 1 cc. of the filtered reagent.

Results.—Artificial honey gives an intense yellow coloration. The depth of color is proportional to the amount present.

9. B-NAPHTHOL TEST, LITTERSHIED (Analyst, 1913, **38**: 217).

Reagent.—88 to 90 per cent sulphuric acid. Redistilled ether.

Manipulation.—Stir 20 grams of honey with 10 cc. of ether, decant and repeat extraction. Transfer ethereal extracts to porcelain dish containing a crystal of B-Naphthol. Treat residue with 5 cc. of the acid. Add acid carefully so that it flows over whole surface of residue.

Results.—If honey contains artificial invert sugar a Bordeaux red or blue violet coloration will appear within 30 minutes. Natural honey gives a dirty yellow color.

Give your conclusions as to the purity of these samples, from the various tests you make on them. Give your opinion as to which ones are adulterated, if any, and which ones are pure, if any.

Before submitting the samples and the tests to the various collaborators, the tests were carried out by the associate referee on five samples of pure honey obtained from authentic sources. In the following instead of reporting the sample as negative or positive, I have indicated the color change that took place.

DESCRIPTION OF SAMPLES.

Sample 1.—Light colored honey gathered in 1913 from clover: extracted with a power extractor in the cold; flavor good.

Sample 2.—Light colored honey, slightly granular, gathered in 1913 from clover; extracted with a power extractor in the cold; flavor good.

Sample 3.—Light colored honey, gathered in 1913 from clover; extracted with power extractor in the cold; flavor good.

Sample 4.—Dark colored honey, gathered in 1911 from buckwheat and heartsease; flavor poor, similar to sorghum. This sample it will be noted has a tendency to give all the reactions for invert sugar. No doubt due to its age, traces of furfural or furfural derivatives have formed.

Sample 5.—Dark colored honey, gathered in 1913 from golden rod; extracted in cold; flavor fair.

Results on pure honey.

SAMPLE NO.	ORIGINAL FIEHE TEST (10 minutes to 24 hours)		REINHARDT'S MODIFICATION (25 PER CENT HYDROCHLORIC ACID (10 minutes to 24 hours)		HALPHEN'S MODIFICATION (ETHER SOLUTION) (10 minutes to 24 hours)		HARTMAN'S MODIFICATION (10 minutes to 24 hours)	
1....	No change	Faint pink	No change	Faint pink	No change	No change	Faint pink	Cherry red
2....	Do	Do	Do	Do	Do	Do	Do	Do
3....	Do	Do	Do	Do	Do	Faint pink	Do	Do
4....	Faint pink	Pink	Faint pink	Pink	Do	No change	No change	Do
5....	No change	Faint pink	No change	Faint pink	Do	Faint pink	Do	Do

SAMPLE NO.	BRYAN'S MODIFICATION	BROWN'S ANILIN ACETATE TEST	FEDER'S ANILIN CHLORID TEST	BENZIDIN ACETATE TEST	B-NAPHTHOL TEST
1........	No change	No change	Faint pink	No change	Dirty yellow
2........	Do	Do	Do	Do	Do
3........	Do	Do	Do	Do	Do
4........	....	Faint red	Faint red	Faint yellow	Faint violet on edges
5........	No change	No change	Faint pink	No change	Dirty yellow

RESULTS OF COLLABORATORS.

Collaborative results on six samples of honey.

SAMPLE AND ANALYST	ORIGINAL FIEHE TEST (10 minutes to 24 hours)		REINHARDT'S MODIFICATION (25 PER CENT HYDROCHLORIC ACID) (10 minutes to 24 hours)		HALPHEN'S MODIFICATION (ETHER SOLUTION) (10 minutes to 24 hours)		HARTMAN'S MODIFICATION (10 minutes to 24 hours)		BRYAN'S MODIFICATION	BROWN'S ANILIN ACETATE TEST	FEDER'S ANILIN CHLORID TEST	BENZIDIN ACETATE TEST	B-NAPHTHOL TEST
SAMPLE A:													
Julius Hortvet and G. A. Parkin	Negative	Negative	Negative	Negative	Negative	Negative (pink)	Negative	Positive	Negative (doubtful)	Negative	Negative	Negative	Negative
C. E. Warriner	Do	Do	Do	Do	Negative (instant dirty yellow)	Negative (light brown)	Do	Positive (cherry red)	Negative	Do	Negative (greenish brown)	Do	Do
N. A. Childs	Do	Do	Do	Do	Negative	Negative	Do	Positive	Do	Do	Negative	Do	Do
W. C. Geagley	Do	Dirty red	Do	Do	Doubtful (pink)	Positive (red)	Doubtful (pink)	Do	Do	Do	Do	Do	Do
W. S. Hubbard	Do	Negative	Do	Do	Negative	Negative	Negative	Do	Do	Do	Do	Do	Do
N. B. Lawrence	Do	Do	Do	Do	Do	Do	Do	Negative	Do	Do	Do	Do	Do
F. L. Shannon	Do	Doubtful (pink)	Do	Doubtful (pink)	Do	Negative (brown)	Doubtful (pink)	Positive	Do	Do	Do	Do	Do
SAMPLE B:													
Julius Hortvet and G. A. Parkin	Positive	Positive	Positive	Positive	Positive	Positive	Positive	Do	Positive	Do	Positive	Positive	Positive
C. E. Warriner[1]	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Do	Negative	Do	Negative	Doubtful	Negative
N. A. Childs	Doubtful	Do	Do	Do	Do	Do	Positive	Do	Positive	Doubtful	Doubtful	Do	Doubtful
W. C. Geagley	Do	Positive	Doubtful	Doubtful (brown)	Doubtful	Positive	Do	Do	Doubtful (pink)	Do	Positive	Do	....
W. S. Hubbard	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Do	Negative	Negative	Negative	Negative	Negative
N. B. Lawrence	Do	Do	Do	Do	Do	Do	Do	Negative	Do	Do	Do	Do	Do
F. L. Shannon	Positive	Positive	Doubtful (faint red)	Positive	Do	Doubtful (pink)	Positive	Positive	Positive	Doubtful (faint red)	Positive	Do	Positive
SAMPLE C:													
Julius Hortvet and G. A. Parkin	Do	Do	Positive	Do	Positive	Positive	Do	Do	Do	Positive	Do	Positive	Do
C. E. Warriner	Negative	Doubtful (faint pink)	Do	Do	Do	Negative	Do	Do	Do	Do	Do	Do	Do
N. A. Childs	Positive	Positive	Doubtful	Negative	Do	Positive	Do	Do	Do	Do	Do	Do	Do
W. C. Geagley	Do	Do	Positive	Positive	Do	Do	Do	Do	Do	Do	Do	Do	Do
W. S. Hubbard	Negative	Negative	Negative	Negative	Negative	Negative	Negative	Do	Negative	Doubtful (pink)	Negative	Doubtful	Do
N. B. Lawrence	Positive	Doubtful	Positive	Doubtful	Do	Do	Do	Negative	Do	Positive (pink)	Positive	Positive (pale yellow)	Do
F. L. Shannon	Do	Positive	Do	Positive	Positive	Positive	Positive	Positive	Positive	Positive	Do	Positive	Do

SAMPLE D:													
Julius Hortvet and G. A. Parkin	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
C. E. Warriner	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
N. A. Childs	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
W. C. Geagley	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
W. S. Hubbard	Do	Do	Do	Do	Negative	Negative	Do	Do	Do	Do	Do	Do	Do
N. B. Lawrence	Do	Do	Do	Do	Positive	Positive	Do	Do	Do	Do	Do	Do	Do
F. L. Shannon	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
SAMPLE E:													
Julius Hortvet and G. A. Parkin	Do	Do	Do	Do	Do	Do	Do	Do	Do	Positive (doubtful)	Do	Do	Do
C. E. Warriner	Do	Do	Do	Negative	Do	Do	Do	Do	Do	Positive	Do	Doubtful	Negative
N. A. Childs	Do	Do	Do	Positive	Do	Do	Do	Do	Do	Do	Do	Positive	Positive
W. C. Geagley	Do	Do	Do	Do	Do	Do	Do	Do	Do	Positive (faint ring)	Do	Do	Positive (blue violet)
W. S. Hubbard	Do	Do	Negative	Doubtful	Negative	Negative	Do	Do	Do	Positive	Do	Positive (light yellow)	Positive
N. B. Lawrence	Negative	Negative	Do	Negative	Positive	Positive	Do	Do	Do	Positive (pink)	Do	Positive (pale yellow)	Do
F. L. Shannon	Positive	Positive	Positive	Positive	Negative	Positive pink	Do	Do	Do	Positive (faint ring)	Do	Positive	Do
SAMPLE F:													
Julius Hortvet and C. A. Parkin	Do	Do	Do	Do	Positive	Positive	Do	Do	Do	Positive	Do	Do	Do
C. E. Warriner	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
N. A. Childs	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
W. C. Geagley	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do
W. S. Hubbard	Do	Do	Negative	Do	Do	Do	Do	Do	Do	Do	Do	Do	Deep green
N. B. Lawrence	Do	Do	Positive	Do	Do	Do	Do	Do	Do	Do	Do	Do	Deep green
F. L. Shannon	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Do	Positive

[1] The label became disarranged during shipment on this sample. Therefore, the results reported herewith are on a sample which I assumed to be B.

Conclusions as to purity of samples.

ANALYST	SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D	SAMPLE E	SAMPLE F
Julius Hortvet and G. A. Parkin	Pure	Adulterated	Adulterated	Adulterated	Adulterated	Adulterated
C. E. Warriner						
N. A. Childs	Pure	Adulterated	Adulterated	Adulterated	Adulterated	Adulterated
W. C. Geagley	Do	Doubtful	Do	Do	Do	Do
W. S. Hubbard	Do	Pure	Pure	Do	Do	Do
N. B. Lawrence						
F. L. Shannon	Pure	Adulterated	Adulterated	Adulterated	Adulterated	Adulterated

COMMENTS OF COLLABORATORS.

Hortvet and Parkin: Test 1.—Not very characteristic when invert sugar is present in small amounts. The color that the reagent takes on serves to hide the results.

Test 2.—The reagent must be freshly prepared and when so prepared seems more sensitive to small amounts of invert sugar than reagent 1

Test 3.—A delicate test, but the intensity of the reaction is about the same on Samples B, C, D, and E, although somewhat greater on Sample F.

Test 4.—Offers a variety of carmine shades, which confuses one when deciding on the amount of invert sugar present. The test requires immediate observation.

Test 5.—Much trouble was experienced with the formation of an ether emulsion. The test did not give as decisive result as 7, 8, or 9.

Test 6.—Gave very poor results, no ring coloration developed for about five minutes and then only a faint and unsatisfactory result.

Test 7.—Seems to be a more conclusive and satisfactory result than any of the first six. The intensity of the color would seem to correspond closely with the per cent of invert sugar present.

Test 8.—Seems to be a good test. The shades of yellow vary with amount of invert sugar present.

Test 9.—Appears to be very sensitive to amount of invert sugar present.

N. A. Childs: From the above tests, it is my opinion that A is a sample of pure honey; B probably contains a very small percentage of adulterant, D, C, E, and F are adulterated, the percentage of adulteration being much higher in D and F than in C and E.

W. C. Geagley: Sample B gave results that were questionable in all tests but Halphen's, Hartman's and Feder's, in which cases the reaction was clear and distinct. In all other tests there would be a question as to the purity of this sample since pure honey sometimes reacts slightly. Sample F contains the largest amount of invert sugar, C next, E next, and D next; B contains a very small amount, if any. A is pure honey. In Bryan's modification of Fiehe's test, I find that an emulsion forms when ether is added to the 50 per cent honey solution and shaken that will not break up. By shaking gently this can be overcome to some extent.

W. S. Hubbard: I considered D, E and F to be adulterated and prefer Hartman's modification of Fiehe's test.

DISCUSSION.

It is quite evident from the reports that artificial invert sugar can readily be detected by most workers when it is present in amounts of 20 per cent or over. When the amount is only 5 per cent, however, some difficulty is experienced. It also seems that the nature of the adulterant has something to do with the possibility of its detection. But very little

difficulty was experienced in detecting the 5 per cent Herzfeld sirup in Sample E, while the majority were doubtful as to the presence of an adulterant in Sample B, although they both contained only 5 per cent of the adulterant. This, I believe, can be explained by the fact that the Herzfeld sirup was made by heating, while the commercial invert sugar was no doubt made in the cold. This fact would also explain the discrepancy in the reports where the depth of color has been used as a basis of judgment for the amount of artificial invert sugar present. It would seem that one cannot use the depth of color as a guide to the amount of adulterant present.

Comparing the original Fiehe's reaction with the various modifications, the only advantage gained by any of the modifications seems to be in the keeping qualities of the reagent. The original Fiehe's reagent turns dark on standing and masks the reaction, although with some experience this feature does not seem to interfere. Some workers have recommended that Fiehe's reaction should be permanent after 24 hours in order to draw positive conclusions, although it must be remembered that samples of pure honey will give a pink coloration on standing. This appears to be a good recommendation, as three obtained positive reactions in Sample B.

Bryan's modification of Fiehe's test seems to have been quite satisfactory in the hands of the collaborators. Three report a positive reaction on Sample B, one doubtful, and three negative. Some difficulty is experienced with the ether emulsion in this test.

Hartman's reaction must be observed immediately to be of any value as a pink color develops in 10 minutes and cherry red in 24 hours on pure honey.

Brown's anilin acetate test gave good results although this reaction cannot be depended upon when the adulterant is less than 5 per cent. Four report negative results with this test on Sample B, while three report doubtful results.

Feder's anilin chlorid test develops a faint pink color on pure samples, although after standing for sometime this disappears. The red color developed in the presence of invert sugar is very pronounced. Three report positive with this test, one doubtful and three negative on Sample B.

The benzidin acetate test and the B-Naphthol test do not seem to have been very satisfactory when the adulterant was only 5 per cent. But one reported a positive reaction with the former test and only two with the latter.

RECOMMENDATIONS.

It is recommended—

That the work be continued for another year, studying the tests which proved the most satisfactory in the hands of all the collaborators, (1)

The original Fiehe test allowing the color to develop for 24 hours; (2) Hartman's modification of the Fiehe test, noting the color immediately after the addition of the reagent; (3) Bryan's modification of Fiehe's test, changing the word "vigorously" to "gently;" (4) Feder's anilin chlorid test: with a view to adopting these as provisional methods in 1915.

REPORT ON FRUITS AND FRUIT PRODUCTS.

By H. C. Gore (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*[1]

ESTIMATION OF MALIC ACID IN FRUIT PRODUCTS.

The work reported last year formed the ground work for further development of the uranyl acetate method of estimation of malic and tartaric acids, and indicated that a new polarimetric method for the estimation of the two acids, using ammonium molybdate instead of uranyl acetate as the activating agent, was in sight.

In addition to the conditions necessary for the successful use of uranyl acetate laid down by Yoder, and those for use of ammonium molybdate indicated by the writer, L. W. Andrews found the time of standing after mixing to be an important factor, and that exposure to daylight must be avoided particularly in case of tartaric acid. In the case of malic acid it is possible to state a general method widely applicable to fruit products and other substances. Two reagents are used in separate solution. Uranyl acetate gives polarizations to the left, ammonium molybdate to the right. Well-agreeing results are usually obtained.

Estimation of tartaric acid using the named reagents has not been worked out. The situation is here more complicated than in the case of malic acid.

GENERAL METHOD FOR MALIC ACID APPLICABLE TO FRUIT JUICES, JELLIES, SIRUPS, AND OTHER FRUIT PRODUCTS, PROBABLY INCLUDING VINEGARS AND WINES.

Determine the amount of free acid present by titrating a portion of the sample with standard alkali and calculate the weight of solid barium hydroxid required to nearly neutralize the free acid.

Add to 25 cc. or 25 grams of sample $2\frac{1}{2}$ to 3 volumes of 95 per cent alcohol; this will precipitate the pectins. With jellies and heavy sirups special precautions have to be observed to prevent loss of malic acid due to imperfect solution of the sample in alcohol or to imperfect washing. Filter off the precipitate with suction and wash well with 95 per cent alcohol. To the filtrate add sufficient powdered barium hydroxid to nearly neutralize the acidity. Stir until reaction is complete

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[1] Read by M. G. Mastin.

and then add three to five drops of an aqueous barium acetate solution containing 50 grams in 100 cc. or more if required, for the purpose of providing an excess of barium. Make up the solution to about 375 cc. with 95 per cent alcohol and digest on the steam bath until the precipitate settles readily after being stirred. Filter with suction in a cup-shaped filter and wash well. Dry the precipitate thoroughly, digest with hot water and make up after cooling to 100 cc. This amount of water is sufficient to dissolve barium malate up to amounts as large as approximately 0.9 gram per 100 cc. Filter and treat separate portions of 25 cc. each as described later.

To this point the method is adapted from part of a method given in a preceding report,[1] there designated as the Yoder method. In its present form it is the result of the work of M. G. Mastin, of the Bureau of Chemistry. He finds this procedure applicable to fruit products containing considerable coloring matter and even to those containing tartaric acid. Where citric acid is present in addition to malic acid, as in orange juice, the results were somewhat higher by the molybdate than by the uranyl acetate method.

URANYL ACETATE PROCEDURE.

Prepare a solution of uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, containing 33.966 grams per liter of the pure salt. The uranium content of the salt should be determined (by ignition to U_3O_8), and if it is a little below the theory (56.18 per cent), a correspondingly greater amount of the acetate is to be taken. If it is several per cent too low, a purer material should be obtained.

Mix 25 cc. of this solution with 25 cc. of the solution of malic acid to be tested, which should be neutral or faintly acid, and should not contain more than 1 gram in 100 cc. of malic acid. Keep in the dark for at least five or preferably ten hours before the final readings are made. Polarize in a 200 mm. tube at or near 20°C., using white light and the bichromate cell. Table 1 gives the concentration of malic acid in the solution polarized:

TABLE 1.

Grams of malic acid per 100 cc. corresponding to optical rotatory power in Ventzke degrees, in presence of uranyl acetate.

°V.	MALIC ACID	DIFFERENCE	°V.	MALIC ACID	DIFFERENCE
200 mm.	*grams per 100 cc.*		*200 mm.*	*grams per 100 cc.*	
1	0.039	0.035	9	0.316	0.034
2	0.075	0.035	10	0.350	0.034
3	0.110	0.035	11	0.384	0.034
4	0.145	0.035	12	0.418	0.034
5	0.179	0.034	13	0.452	0.034
6	0.214	0.034	14	0.486	0.034
7	0.248	0.034	15	0.519	0.034
8	0.282	0.034			

[1] Bur. Chem. Bul. 162, pp. 65–66.

AMMONIUM MOLYBDATE PROCEDURE.

Prepare a solution of ammonium heptomolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, containing 172.8 grams per liter of molybdenum trioxid. For this 212 grams of the pure salt are sufficient, but more or less of the salt at hand may be required according to purity and content of water of crystallization. Also prepare a solution containing 300 grams of acetic acid per liter.

Mix 20 cc. of the above solution of ammonium molybdate with 25 cc. of the solution of neutralized malic acid to be examined, in a 50 cc. flask, make up the volume with the solution of acetic acid, and allow to stand in the dark for about 4 hours. Polarize as directed above. Table 2, worked out by Andrews, gives the concentration of malic acid corresponding to the polarization:

TABLE 2.

Rotations of malic acid in ammonium molybdate solutions.

°V	MALIC ACID	DIFFERENCE	°V	MALIC ACID	DIFFERENCE
200 mm.	*grams per 100 cc.*		*200 mm.*	*grams per 100 cc.*	
1	0.027	0.024	21	0.496	0.023
2	0.052	0.024	22	0.519	0.023
3	0.077	0.023	23	0.542	0.023
4	0.100	0.023	24	0.565	0.023
5	0.124	0.023	25	0.588	0.023
6	0.148	0.023	26	0.611	0.023
7	0.171	0.023	27	0.634	0.023
8	0.195	0.023	28	0.657	0.022
9	0.218	0.023	29	0.680	0.023
10	0.241	0.023	30	0.703	0.022
11	0.264	0.023	31	0.726	0.023
12	0.288	0.023	32	0.749	0.022
13	0.311	0.023	33	0.772	0.023
14	0.334	0.023	34	0.795	0.022
15	0.357	0.023	35	0.818	0.022
16	0.381	0.023	36	0.841	0.022
17	0.404	0.023	37	0.864	0.022
18	0.427	0.023	38	0.886	0.022
19	0.450	0.023	39	0.909	0.022
20	0.473	0.023	40	0.932	0.022

TABLE 2.—*Concluded.*

°V	MALIC ACID	DIFFERENCE	°V	MALIC ACID	DIFFERENCE
200 mm.	*grams per 100 cc.*		*200 mm.*	*grams per 100 cc.*	
41	0.955	0.022	66	1.526	0.022
42	0.879	0.022	67	1.549	0.022
43	1.001	0.022	68	1.572	0.022
44	1.024	0.022	69	1.595	0.022
45	1.047	0.022	70	1.616	0.022
46	1.070	0.022	71	1.640	0.022
47	1.092	0.022	72	1.663	0.022
48	1.115	0.022	73	1.686	0.022
49	1.138	0.022	74	1.708	0.022
50	1.161	0.022	75	1.731	0.022
51	1.184	0.022	76	1.754	0.022
52	1.207	0.022	77	1.777	0.022
53	1.229	0.022	78	1.800	0.022
54	1.252	0.022	79	1.822	0.022
55	1.275	0.022	80	1.845	0.022
56	1.298	0.022	81	1.868	0.022
57	1.321	0.022	82	1.891	0.022
58	1.344	0.022	83	1.913	0.022
59	1.366	0.022	84	1.936	0.022
60	1.389	0.022	85	1.958	0.022
61	1.412	0.022	86	1.982	0.022
62	1.435	0.022	87	2.004	0.022
63	1.458	0.022	88	2.027	0.022
64	1.481	0.022	89	2.050	0.022
65	1.503	0.022	90	2.073	0.022

This method was sent out with samples to a number of collaborators. A summary of the results of the work of several is given in the following table:

TABLE 3.

Determination of malic acid in fruit juices.

ANALYST	CIDER		PEACH JUICE	
	Uranyl acetate	Ammonium molydate	Uranyl acetate	Ammonium molybdate
	per cent	*per cent*	*per cent*	*per cent*
A. W. Broomell, Washington, D. C.......	0.60	0.530	0.74	0.74
	0.60	0.530	0.71	0.82
	0.60	0.550	0.77	0.82
M. G. Mastin, Washington, D. C.........	0.60	0.616	1.07	1.10
	0.60	0.616	1.07	1.10
	....	....	1.03	1.09

ESTIMATION OF CITRIC ACID.

Up to the present time no wholly satisfactory method of estimating citric acid is known, despite the fact that much attention has been given to the problem. Andrews made a discovery which leads to a new method. At the suggestion of the writer, he tried the effect of the presence of citrates on the polarizations of malic acid in presence of acetic acid and salt of molybdic acid. It was expected that where less molybdate was present than enough to combine with both acids, lowerings of the readings would be observed in consequence of the fact that the molybdenum would be partitioned between the two oxyacids. This, Andrews found to be the case. He found, however, that when more than sufficient molybdenum was present for both acids, large increases in polarizations were observed over the increases which occurred with malic acid alone. Mastin later finds that this observation is probably specific for citric acid. Sodium salts of succinic, lactic and aconitic acids produced no effect on the molybdenum malic acid polarizations. This observation of Andrews was promptly developed by him into a method using, however, sodium molybdate, a somewhat unusual reagent. He found that the polarization increases due to citrates did not vary directly with the amounts present but that the variations were, however, regular, and he constructed curves from which the amounts present of citric acid could be determined, using appropriate solutions containing sodium molybdate, sodium malate, and free acetic acid. If the solutions, to be tested already contained malates, the amounts present could be estimated from the polarizations with uranyl acetate, and necessary additional amounts could then be added so that the solutions contain the required amount of malic acid. Mastin is now working out the procedure for estimation of citric acid, using ammonium molybdate. For the assay of citrates and citric acid, a very simple procedure can undoubtedly be developed. In fruit products the method will necessarily be more complicated.

RECOMMENDATIONS.

It is recommended—

(1) That the proposed methods for malic acid be provisionally adopted by the association, and that the referee for the coming year be instructed to develop these methods further.

(2) That the method for the estimation of citric acid by the use of a solution containing ammonium molybdate, sodium malate, and acetic acid, be further studied.

REPORT ON WINE.

By B. G. Hartmann (Bureau of Chemistry Food and Drug Inspection Laboratory, Chicago, Ill.), *Associate Referee.*

This year's work on wine was devoted to a further study of the methods for determining tartaric acid in wines and grape juices. The work was planned in accordance with the resolutions on the subject adopted at the last meeting of the association.

The following instructions to the collaborators show the purpose and scope of the plan:

INSTRUCTIONS TO COLLABORATORS.

DETERMINATION OF TARTARIC ACID IN PRODUCTS CONTAINING FREE PHOSPHORIC ACID.

The three solutions submitted for this year's work on tartaric acid contain varying amounts of tartaric acid and phosphoric acid. In order that products similar to those found in the market might be had, sugar, alcohol and coloring were added to the solutions. The solutions are marked 1, 2 and 3. It is suggested that the total tartaric acid be determined in each of the solutions, according to (1) The bulletin method, described on page 86 of Bulletin 107, Revised; (2) method proposed by Hartmann and Eoff, one-half neutralized; (3) method proposed by Hartmann and Eoff, completely neutralized.

Before starting the work, it is suggested that collaborators read "Proposed Method for the Determination of Tartaric Acid Content in Wines and Grape Juices," Bulletin 162, page 71.

PRELIMINARY PROCEDURE.

Although no precipitate is expected to occur in the solutions, it seems advisable, as a precautionary measure, to filter before proceeding with the determinations.

Determining the acidity of the samples.—The indicator to be used is prepared by thoroughly mixing in a mortar 0.5 gram of phenolphthalein and 50 grams of sodium sulphate. Into the cavities of a spot plate, place about 0.1 gram of the indicator. Measure 20 cc. of the sample into a 250 cc. beaker and titrate in the cold with tenth-normal sodium hydroxid until a few drops spotted on the indicator give a purple tint. It is essential, in order to get a good, clean end point that during spotting none of the indicator is carried into the solution undergoing titration. Place the indicator to one side of cavity and allow the drops to run into the indicator. It will be found that the red color of the sample does not interfere and that, with a

little practice, a very satisfactory end point is obtained. This indicator is especially adapted to phosphoric acid. It has been found that phosphoric acid solutions may be accurately titrated, giving sodium di-acid phosphate. The collaborators are requested to give special attention to the behavior of this indicator, since it has been found that its use is applicable to a wide range of deeply-colored products. In case difficulty is experienced with this indicator, it is suggested that any other means of arriving at the acidity of the samples be used.

Express the acidity in terms of tartaric acid per 100 cc. 1 cc. N/10 NaOH = 0.0075 gram tartaric acid.

DETERMINATION OF TARTARIC ACID.

(1) *Bulletin method.*—Transfer 50 cc. of the solution at 20°C. to a 250 cc. beaker, add 50 cc. of distilled water, and follow procedure described on page 86 of Bulletin 107, Revised, using 20 cc. of alcohol instead of 15 cc.

(2) *Method proposed by Hartmann and Eoff (one-half neutralized).*—Transfer 50 cc. of solution at 20°C. to a 250 cc. beaker; add required amount of normal sodium hydroxid to neutralize one-half of the acidity; add enough water to make 100 cc. Proceed as in bulletin method, omitting the addition of potassium acetate and using 20 cc. of alcohol instead of 15 cc.

(3) *Method proposed by Hartmann and Eoff (completely neutralized).*—Transfer 50 cc. of the solution at 20°C.to a 250 cc. beaker and add required amount of normal sodium hydroxid to just neutralize the acidity of the 50 cc. solution used and add enough distilled water to make 100 cc.; add pure tartaric acid; pulverize the tartaric acid and dry at 100°C. for 2 hours. Keep in a glass stoppered bottle in a desiccator. The amount of tartaric acid to be added is found by multiplying by 0.075 the number of cubic centimeters of normal sodium hydroxid used to neutralize the 50 cc. sample. Weigh this amount exactly. When the tartaric acid is dissolved proceed as in bulletin method, omitting the addition of potassium acetate and using 20 cc. of alcohol instead of 15 cc. Subtract the tartaric acid added from the total tartaric acid found by titration. This gives the actual amount of tartaric acid present in the 50 cc. sample taken.

It is, of course, necessary to multiply the figures obtained in the different determinations by 2, in order to get the amount of tartaric acid contained in the solutions.

Instead of allowing the reaction mixture "to stand at room temperature for at least 15 hours," as given in the bulletin method, hold for this time at a temperature not exceeding 15°C.

The following is the composition of the three solutions in grams per 100 cc.:

DETERMINATION	1	2	3
Acid, as tartaric	4.92	2.52	1.96
Total tartaric acid	2.00	1.80	1.89
Phosphoric acid	1.91	0.48	0.048
Caramel	1.2	1.2	1.2
Amaranth	0.024	0.024	0.024
Cane sugar	5.0	5.0	5.0
Alcohol	5.0	5.0	5.0

RESULTS OF COLLABORATION.

The following are the results obtained by the collaborators on the three solutions:

Analytical results on tartaric acid in three solutions.

SOLUTION AND COLLABORATOR	DATE ANALYZED	ACID AS TARTARIC	TOTAL TARTARIC ACID		
			Method 1	Method 2	Method 3
SOLUTION 1:					
B. G. Hartmann	7/20/14	4.89 4.91 4.91	0.70 0.78 0.73	1.87 1.88 1.89	1.89 1.90 1.90
E. H. Berry	8/12/14	4.77 4.77	0.64 0.69 0.68	1.67 1.69 1.71	1.82 1.82 1.87
J. R. Eoff	8/24/14	4.80	0.06 0.24	1.53 1.56	1.76 1.76 1.77
R. C. Kent	8/26/14	4.71 4.71 4.71	0.63 0.61 0.56	1.66 1.66 1.67	1.68 1.67 1.67
M. J. Ingle	10/30/14	5.06	0	1.61	1.65
SOLUTION 2:					
B. G. Hartmann	7/20/14	2.57 2.57 2.55	1.02 1.02 1.04	1.76 1.75 1.76	1.75 1.77 1.75
E. H. Berry	8/12/14	2.48 2.48	0.89 0.91 0.91	1.63 1.63 1.61	1.66 1.69 1.69
J. R. Eoff	8/24/14	2.47	0.67 0.67	1.50 1.52	1.61 1.63 1.60
R. C. Kent	8/26/14	2.45 2.45 2.44	0.89 0.93	1.57 1.57 1.58	1.58 1.58
M. J. Ingle	10/30/14	2.51	0.65	1.51	1.63
SOLUTION 3:					
B. G. Hartmann	7/20/14	2.00 1.99 1.99	1.21 1.23 1.24	1.87 1.86 1.87	1.86 1.87 1.88
E. H. Berry	8/12/14	1.95 1.95	1.19 1.19 1.10	1.77 1.77 1.76	1.76 1.77 1.78
J. R. Eoff	8/24/14	1.93	1.05 0.95	1.68 1.69	1.78 1.77 1.77
R. C. Kent	8/26/14	1.92 1.91 1.92	1.22 1.21 1.22	1.72 1.72 1.71	1.71 1.71 1.71
M. J. Ingle	10/30/14	1.95	0.92	1.63	1.67

NOTES BY THE COLLABORATORS.

E. H. Berry.—I found it necessary to break the filter paper up as much as possible before titrating the tartaric acid as the paper holds the acid. The indicator was found to be very satisfactory. In highly-colored solutions where with phenolphthalein solution it is practically impossible to detect the end point, with the indicator used in this work, it is possible to detect it to within 0.1 or 0.2 of a cubic centimeter of tenth-normal alkali.

B. G. Hartmann.—The indicator proposed for this work is very satisfactory. It was found that the addition of a few cubic centimeters of alcohol to the mixture undergoing titration helps materially. The alcohol allows a better and more uniform penetration into the indicator during spotting. Also it was found that if the indicator is too fine, the penetrating power is decreased to such an extent that great difficulty is experienced in spotting.

M. J. Ingle.—For ordinary routine work the half-neutralized method seems to be practicable enough, especially in cases where the addition of tartaric acid is not needed to help the precipitation. A procedure found to be of help in making the end reaction on the tile plate more easily visible, was to put an equal amount of the anhydrous sodium sulphate alongside of the indicator in the same depression. Then, by allowing the drop of solution to wet both portions of the powder, the contact between the sulphate blank and the indicator renders it more sensitive. To those having difficulty in using an inside indicator in the dyed-bitartrate solution, it was found practicable to concentrate the color from this solution on wool introduced into it. By previously boiling and washing this wool any acidity present is eliminated. Then by allowing the aqueous solution of the bitartrate precipitate to stand on the water bath for an hour or so with an excess of the washed wool, the color is removed. Titrate with the wool in the beaker.

R. C. Kent.—The indicator is very good for titrating highly colored solutions. The end point is easily distinguished with 0.1 cc. tenth-normal sodium hydroxid.

DISCUSSION.

The reports by the various collaborators show that the bulletin method is entirely unreliable and useless in cases where free phosphoric acid is present. Two of the collaborators report no tartaric acid in Solution 1 when the bulletin method was used. This is undoubtedly the true result obtained by adhering literally to the instructions issued. The bulletin method calls for one minute of stirring to start crystallization of potassium acid tartrate. In a solution containing a high amount of free phosphoric acid, this time of stirring is too short to start precipitation. That the other collaborators found tartaric acid in Solution 1 is due to the fact that longer time of stirring was used.

Methods 2 and 3 (Hartmann and Eoff, one-half neutralized and completely neutralized) although giving fairly good results, are far from satisfactory. That these methods did not give better results is due to the well known fact that alcohol and tartaric acid combine to form esters and this esterification is further augmented by the phosphoric acid content which acts as a catalizer. The esters form rapidly and increase with time,

as will be seen from the report, causing a gradual decrease in tartaric acid found, from 0.2 to 0.3 gram in 3 months.

For the purpose of saponifying the esters, 50 cc. of each of the solutions were neutralized with sodium hydroxid and 3 cc. of normal sodium hydroxid added in excess, and the solution allowed to stand overnight. The volume was then made up to 100 cc. with water, the required amount of tartaric acid added, and the determination proceeded with as described under Method 3. This procedure gave the following results:

Total tartaric acid (grams per 100 cc.)

SOLUTION	CONTAINED	B. G. HARTMANN 8/26/14	J. R. EOFF 10/17/14	J. R. EOFF 10/26/14
1	2.00	2.00 2.00 2.00	2.05	2.08 2.09
2	1.80	1.78 1.77 1.79	1.83	1.84 1.82
3	1.89	1.88 1.89 1.89	1.92	1.89 1.89

From these results it appears that in order to arrive at the true total tartaric acid content in alcoholic mixtures, saponification of esters must precede the final determination. In order to verify these findings, it was suggested to J. R. Eoff to apply the procedure to the solutions. His results agree very well with the results obtained by the association referee and are given in the above table.

The reports on the behavior of the proposed indicator are very encouraging. From experiments made with it, there can be no doubt that its use is of unlimited application in work on highly-colored organic acid solutions. Experiments with the indicator on phosphoric acid solutions of known content gave excellent results, the end point being very sharp when the solution undergoing titration was kept cold.

RECOMMENDATIONS.

It is recommended—

(1) That the following method for determining the total tartaric acid content in solutions containing free mineral acids or alcohol be subjected to further study: Neutralize the acidity with sodium hydroxid and add 3 cc. of normal sodium hydroxid in excess. Allow to stand overnight and add the required amount of tartaric acid (0.075 gram for every cubic centimeter of normal sodium hydroxid added). After the tartaric acid has

dissolved, add 2 cc. of glacial acetic acid and 15 grams of potassium chlorid. When the salt has gone into solution, add 20 cc. of alcohol and stir until precipitation sets in. Allow to stand overnight at a temperature not to exceed 15°C. Collect the crystals and titrate in the usual manner.

(2) That the indicator described be tried on other food products.

MARASCHINO.

By J. G. Riley and A. L. Sullivan. (Bureau of Chemistry Food and Drug Inspection Laboratory, Boston, Mass.).[1]

The world-famed cordial, maraschino, was first manufactured commercially early in the eighteenth century in Zara, Dalmatia, from the marasca cherry, a small variety of the European wild cherry native to the Dalmatian mountains. The manufacture of this cordial has continued to the present day and large quantities of maraschino are still shipped from Dalmatia. The superior excellence of maraschino led to the manufacture of similar cordials in the countries of Italy, France, Holland, and America.

The purpose of this paper is to set forth analyses of ten samples of genuine maraschino, representing the products of six manufacturers, obtained through the courtesy of the American Consul at Trieste, Austria, and Mr. Nicolo Luxardo. Analyses of commerical samples of maraschino manufactured in Holland, France, and the United States are also tabulated.

METHODS OF MANUFACTURE.

In Dalmatia during the month of June, marasca cherries are gathered and shipped to Zara. For the manufacture of the best grade maraschino the cherries are pitted, crushed, and allowed to ferment for 4 or 5 days with a small quantity of leaves from the marasca cherry tree; from 10 to 15 per cent pure alcohol is then added to arrest fermentation and to prevent the development of wild yeasts and bacteria. One of the objects of adding alcohol to the fermented cherries is to enable the manufacturer to distill the product at his leisure throughout the year. If the fermented cherries are allowed to stand any length of time there is danger of serious deterioration in the flavor and aroma of the product, especial y when alcohol has not been added. The fermented cherries do not yield sufficient alcohol for proper preservation of the mass.

Simple pot stills are used exclusively in the distillation of maraschino spirit and these in most cases are heated by direct fire, although at the present time the use of stills heated by steam coils is being introduced. The type of the still, however, remains practically the same as the original pot still. The first and last portions of the distillate are rejected for the

[1] Read by C. S. Brinton.

best grades of maraschino, and a portion of a distillate coming over at about 140 proof collected. The strong alcoholic distillate is stored either in glass-lined barrels or cisterns, or in barrels which have been treated so that the spirit will not extract any color from them. The aim of the manufacturer is to age the distillate when possible for from two to three years. The maraschino cordial as found on the market is made by diluting a certain amount of the strong maraschino spirit with sirup. There is some question as to whether any flavoring materials other than the cherries and leaves are used. The best manufacturers claim to use no artificial flavor. Lower grades of maraschino liqueur are produced from cherries which are more or less unsound and in some cases the pits are not removed so that the distillate may show appreciable traces of hydrocyanic acid. It is claimed by the manufacturers of the genuine Dalmatian maraschino that the best product is made from the wild marasca cherry. If the cherry is transplanted to other localities and countries and cultivated it will not yield upon distillation a product having the flavor of the original fruit.

In France so-called maraschino is made by various methods, which may briefly be classified under three heads:

(1) The cherries are crushed and allowed to undergo alcoholic fermentation in the presence of a certain amount of the cherry leaves. After the fermentation the product is distilled and either a very strong spirit known as marasca spirit containing 40 to 50 per cent alcohol collected, or the fermented cherries are distilled in such a manner that a dilute spirit, 8 to 15 per cent alcohol strength, is obtained. This is called eau de marasque or marasca water.

(2) A mixture of black cherries, raspberries, or other fruit and cherry leaves, with a small amount of peach kernels and iris is fermented and distilled and a strong distillate obtained which is used for the manufacture of the cordial.

(3) Essences of peach kernels, orange flowers, jasmine, and vanilla are mixed with pure alcohol and an artificial spirit obtained which is later made into a cordial.

The method described under (1) is generally similar to that followed in Dalmatia. It is claimed that the cherries used are of the same variety as the original marasca cherries and that these cherries grow in Italy, Greece, and France as well as in Dalmatia. From information obtained from various sources it appears that it is well recognized in France that the marasca spirit or marasca water obtained from the native wild cherry is distinctly inferior in flavoring strength and quality to that produced in Dalmatia. Information from similar sources makes it evident that genuine marasca distillate from Dalmatia is often claimed to be used by French manufacturers.

In Holland so-called maraschino has been manufactured for many years; the following statements were made by a Dutch manufacturer:

"In the trade, the term 'Maraschino' means a liqueur produced by the distillation of the kernel of stone fruit, generically the *Prunus acidus;* it may be simply the cherry, or the May Cherry, the black cherry, Morello, or Marasque. It is said that this general variety of cherry originated in the eastern and southern countries of Europe where the Marasque kind has predominated.

"It is believed that in the beginning, over a century ago, the Marasque was the sole or chief variety of cherry from which Maraschino was made. But in course of time, it is related, to suit the public taste, this liqueur was distilled by producers all over Europe, from other varieties of the cherry as well as the Marasque—sometimes blending Marasque and other kinds, sometimes using no Marasque whatever. Sometimes, also, other substances were added, as flavoring, to please the consumer. All this time the liqueur was called Maraschino, and thus this became a generic term, without specific reference to the Marasque or Marasca cherry.

"At the present time, as appears from the best information obtainable, no maker of Maraschino in this country uses cherries brought from Dalmatia, but the makers do use local or other varieties as near like them as possible. For instance, the X firm inform me that they use cherries grown in this country from real Marasca sprouts which they import and plant here.

"The member of the firm of X says that the flavor of his Maraschino is reenforced by other substances * * * these substances are a trade secret which he could not divulge."

The following table gives the analysis of ten samples of genuine Dalmatian maraschino, nine samples of the French product, four samples of the Dutch product, and three of the American; also a composite analysis of Kirschwasser taken from König, volume 1, page 1514.

Description of Samples Analyzed.

2216-K to 2221-K. Characteristic flavor and aroma of true maraschino. Slight suggestion of Kirsch.

2222-K. Weak flavored, no maraschino flavor; very little, if any, cherry distillate; test for hydrocyanic acid not regarded as conclusive.

2223-K. Cherry kernel flavor; benzaldehyde odor noticeable on diluted sample.

2227-K and S. F. 3249. Flavor very weak, possibly derived from wild cherries.

NY. 38512. Nearly all spirit, with a slight flavor of maraschino.

NY. 38513. Spirits flavored (rose and syringa suspected); consular report shows that in district where sample was made alcohol and artificial flavors are used with either Zara marasca water, or same from Grasse district, France.

NY. 38752. Weak flavored, may contain a small amount of maraschino.

NY. 39752. Does not have flavor of maraschino; may contain a cherry distillate; benzaldehyde suspected by odor and taste; manufacturer admitted later that sample was not prepared from marasca cherries.

2224-K and NY. 26099. Perfumed odor rose present.

2225-K and NY. 26047. Artificial flavor present; no maraschino flavor; see description of Dutch maraschino.

2226-K. No maraschino flavor; benzaldehyde suspected by odor and taste; made from cherries, pits, alcohol, etc.

3550-H. No flavor of maraschino.

1687-K. Has maraschino flavor; use of imported marasca distillate suspected.

The analysis of genuine Dalmatian maraschino shows it to be an alcoholic cordial containing from 30 to 44 per cent of alcohol, and 26 to 36 per

Analysis of the spirits of Maraschino.

VARIETY	SPECIFIC GRAVITY AT 15.6°	ALCOHOL (Per cent by volume)	SOLIDS BY SPINDLE (Per cent)	PARTS PER 100,000, 100° PROOF (50 PER CENT ALCOHOL) Acids as acetic	Esters as ethyl acetate	Aldehydes	Furfural	Fuel oil as amyl alcohol (Allen Marquard method)	Total congenerics	BENZALDEHYDE (Parts per 100,000,100° proof)	HYDROCYANIC ACID BY Guaiac copper test	Sulphocyanate test
GENUINE DALMATIAN MARASCHINO:												
2216-K	1.066	37.62	26.1	4.0	15.7	4.3	0.0	27.7	51.7	Trace	Very faint	Negative
2217-K	1.091	32.73	29.9	9.1	9.9	3.2	0.32	62.0	84.5	5.1	Positive	Positive
2218-K	1.096	31.29	30.5	4.8	4.9	7.9	0.0	9.6	27.2	2.2	Negative	Negative
2219-K	1.067	44.59	28.5	10.0	30.8	8.5	0.23	33.8	83.3	3.4	Positive	Trace
A[1]	1.105	33.3	35.9	0.2	12.9	3.7	0.18	13.6	30.3	...	Do	...
B[1]	1.095	35.48	34.9	13.8	25.8	8.4	0.52	25.3	73.8	...	Negative	...
C[1]	1.067	42.06	31.5	18.5	26.6	8.8	0.59	56.4	110.8	...	Do	...
2220-K	1.106	35.29	33.6	2.5	29.4	6.4	0.0	31.8	70.1	3.4	Very faint	Negative
B[1]	1.106	30.94	34.27	6.4	122.8	28.2	Trace	55.4	212.8	...	Trace	Do
2221-K	...	32.40	31.1	9.2	46.3	2.0	0.0	Trace	57.5	Negative	Negative	Do
Maximum	1.106	44.59	35.9	18.5	122.8	28.2	0.59	62.0	212.8	5.1	...	...
Minimum	1.066	30.94	26.1	0.2	4.9	2.0	0.0	Trace	27.2	2.2	...	...
FRENCH:												
2222-K	1.116	29.84	34.3	5.0	0.0	1.6	0.0	3.6	10.2	Negative	Faint trace	Negative
2223-K	1.095	38.31	32.3	7.8	15.1	1.39	0.27	30.8	55.3	26.4	Positive	Positive
2227-K	1.204	18.66	52.7	12.0	9.4	0.9	0.0	14.1	36.4	Doubtful	Faint trace	Negative
S. F. 3249[1]	...	19.15	49.9	...	0.0	4.2	...	17.8	...	...	Negative	Do
NY. 38512[1]	1.138	27.56	47.9	...	27.2	1.88	0.0	...	...	None	...	None
NY. 26048[1]	...	27.42	45.9	...	20.0	1.8	Meretrace	22.7	...	...	Faint	...
NY. 38513[1]	1.093	28.42	35.3	...	11.6	0.01	0.0	...	...	None	None	None
NY. 38752[1]	1.105	30.4	38.7	...	47.3	0.0	0.0	...	...	Do	Do	Do
NY. 39751[1]	...	26.2	...	22.	61.	8.6	...	67.	...	10.6	...	None detected
DUTCH:												
2224-K	1.108	32.59	33.3	4.6	9.0	2.3	0.0	35.4	51.3	18.2	Positive	Positive
NY. 26099[1]	...	24.85	...	...	15.9	0.8	0.0	33.1	...	...	Faint	...
2225-K	1.143	33.75	40.5	4.4	16.3	4.7	0.0	104.	129.4	16.0	Present	Present
NY. 26047[1]	...	36.05	47.3	...	57.8	4.8	Trace	67.9	...	...	Positive	...
AMERICAN:												
2226-K	1.156	33.38	43.0	44.9	28.0	2.4	0.3	13.1	88.7	25.2	Present	Present
3550-K	1.121	30.50	36.0	4.9	1.8	2.4	0.4	3.6	13.1	9.0	Positive	Positive
1687-K	...	25.15	38.4	5.9	11.0	0.9	0.0	17.5	35.3	Negative	Faint trace	Do
KIRSCHWASSER:												
König, v. 1, p. 1514	...	...	...	45.8	87.4	4.9	0.4	62.2	200.7	...	...	...

[1] Analyzed 1909-1913 by A. L. Sullivan.

cent of solids (sugar). The analysis of the distillates show a comparatively small amount of congenerics. Judging from these analyses it is evident that either the maraschino spirit is very highly rectified or it contains added neutral spirit. This conclusion is strengthened by comparing the analyses of maraschino with Kirschwasser, which is a true cherry distillate. In the case of Kirschwasser the total congenerics average about 200, whereas in the case of maraschino they average 80. It is a well-known fact that pure alcohol is used in the manufacture of maraschino and the low amount of congenerics is explained by this fact. Under the circumstances there is no evidence of the use of rectifying columns in the process of distillation. The analyses show further that maraschino contains very small amounts of benzaldehyde, from traces up to five parts per hundred thousand per 100 proof. Hydrocyanic acid was found present in very small amounts in some of the genuine samples. There is nothing particularly characteristic about the chemical analysis of maraschino which would enable one to judge from the analysis alone whether a given sample is pure.

The most striking feature about the Dalmatian maraschino is the flavor, which can not be measured by a chemical analysis. The peculiar fragrance and delicacy of flavor of genuine maraschino is distinctly different from that of the French, Dutch, and other products. The analyst must draw his conclusions largely from the aroma and taste of the product. The presence of traces of benzaldehyde and hydrocyanic acid indicates a cherry distillate.

Samples marked A, B and C under Dalmatian maraschino are interesting. They were made by the same concern. A is the cheapest product and C is the highest priced. The amount of congenerics in A is 30.3 and in C, 110.8. It is apparent from the analysis that C contains a greater proportion of true marasca distillate than A. Sample 2220-K and Sample B immediately under that number were made by the same concern. The first sample was obtained in 1911 and the second sample in 1912. Sample 2220-K apparently has more of the true marasca distillate than the latter sample.

Examination of French maraschino shows chemical results quite similar to those obtained on the Dalmatian product. Two of the samples, however, contained much larger amounts of benzaldehyde. None of the samples had the characteristic strength and delicacy of flavor of the genuine maraschino. While it is probable that several of them were made from cherry distillates they do not have the strength and delicate flavor of the Dalmatian product. If a distillate made from French cherries was used it is very evident that this product does not have the quality of the Dalmatian product. Another striking feature about the French samples

as a whole is that they are weak flavored, which is probably due to the use of a large percentage of neutral alcohol.

Four samples of Dutch products were examined, representing two different manufacturers. They contain appreciable amounts of benzaldehyde, 16 to 18 parts per 100,000 proof. The flavor is entirely different from that of the Dalmatian product. The presence of benzaldehyde and hydrocyanic acid indicate that the products may have been prepared from cherries. The somewhat excessive amount of benzaldehyde may be accounted for by the use of almond kernels, cherry stones, or some other product yielding benzaldehyde. It is possible that the cherrystones were crushed in the manufacture of the cordials. The four samples undoubtedly were prepared from a fermented product.

The three samples of American manufacture were apparently prepared from cherries and two of them contain appreciable amounts of benzaldehyde, considerably more than is found in the Dalmatian product. Sample 1687-K seems to have the genuine flavor of maraschino, although not particularly strong.

CONCLUSIONS.

Dalmatian maraschino as prepared from the marasca cherry has a delicate fragrance and aroma and a distinctive flavor which is different from products prepared from other varieties of cherries and fruits. Such maraschino may contain traces of benzaldehyde and hydrocyanic acid. The amount of congenerics, that is, the sum of acids, ether, aldehydes, furfural and fusel oil is low, indicating the use of alcohol in the manufacture of the product.

Dalmatian maraschino is not made solely from straight cherry distillate, but contains added spirit. The French, Dutch, and American products generally have an entirely different flavor from the Dalmatian product. In some cases artificial flavoring substances are present. In cases where the flavor has a resemblance to the genuine Dalmatian product the cordial is very weak flavored, that is, does not contain an appreciable amount of genuine maraschino distillate used in its manufacture.

The methods of analysis used were similar to the official methods for the analysis of distilled spirits. Owing to the high sugar content of maraschino it was necessary to dilute the same with water before distilling; 400 cc. was diluted with 200 cc. of water and 500 cc. of distillate was collected. This spirit was analyzed for acids, esters, etc. Benzaldehyde was determined by the Dennis and Dunbar method. Hydrocyanic acid was tested for by the guaiac copper and the sulphocyanate test, as described in Autenrieth.

Genuine maraschino when diluted with water and saturated with sodium bisulphite and extracted with ether imparts its original odor to the ether.

If the ether is carefully evaporated at a low heat the aroma of the original product can be detected. This test is useful where the benzaldehyde flavor is strong, as the sodium bisulphite fixes the benzaldehyde and allows the removal of other flavors by the means of ether.

No reports were made by the associate referees on beer and distilled liquors.

REPORT ON VINEGAR.

By E. H. Goodnow (Bureau of Chemistry Food and Drug Inspection Laboratory, St. Paul, Minn.), *Associate Referee.*

The referee work on vinegar for this year has been confined to a co-operative study of Methods 6, 11, 15, 16 and 17, as given in the 1911 proceedings, Bureau of Chemistry Bulletin 152, page 126. To each member of the association who had indicated a desire to participate in the collaborative work, a sample of cider vinegar was submitted with the following directions for the analytical procedure.

METHODS OF ANALYSIS.

6. Solids.—Measure 10 cc. of filtrated vinegar into a tared flat-bottom platinum dish of 50 mm. diameter, evaporate on the water bath to a thick sirup, and dry for exactly two and one-half hours in the drying oven at the temperature of boiling water; cool and weigh. It is essential to use a flat-bottom dish.

11. Ash.—Measure 25 cc. into a tared platinum dish, evaporate to dryness on the steam bath, heat in the muffle at low heat to expel inflammable gases, treat the charred portion with a few cubic centimeters of water, and evaporate dry on the bath; replace in the muffle at low redness for 15 minutes and continue the alternate evaporation and heating until a white or gray ash is obtained, at no time allowing the temperature to exceed a dull red; cool in desiccator and weigh.

15. Fixed acid.—Measure 10 cc. into a 200 cc. porcelain casserole, evaporate just to dryness, add 5 to 10 cc. of water, and again evaporate; repeat until at least five evaporations have taken place and no odor of acetic acid can be detected. Add nearly 200 cc. of recently-boiled, distilled water and titrate with tenth-normal alkali, using phenolphthalein. One cubic centimeter of tenth-normal alkali is equivalent to 0.0067 gram of malic acid.

16. Volatile acid.—Calculate the fixed acid as acetic and deduct from the total acid. Express as acetic acid.

17. Lead precipitate.—To 10 cc. in a test tube, add 2 cc. of normal lead acetate (20 per cent solution), shake, and let stand one-half hour. Express as turbidity, light, medium, heavy or very heavy.

RESULTS OF COLLABORATION.

The results of the collaborative analyses are given in the following table:

Results of coöperative analysis of a sample of cider vinegar by the methods given above.

ANALYST	SOLIDS	ASH	FIXED ACID	VOLATILE ACID	LEAD PRECIPITATE
	per cent	*per cent*	*gram*	*per cent*	
Nan A. Childs, Lansing, Mich.	2.27 2.24	0.34 0.33	0.077 0.074	5.62	Heavy.
	grams	*gram*		*grams*	
J. O. Clark, Atlanta, Ga.[1]	2.04	0.34	0.10	5.42	Do.
E. R. Lyman, Seattle, Wash.	2.268 2.246	0.3416 0.3380	0.060 0.060	5.376 5.388	Heavy turbidity.
W. B. White, Ithaca, N. Y.	2.251 2.259	0.328 0.325	0.05 0.05	5.40 5.40	Medium (0.3 cc.). Heavy turbidity in supernatant liquid.
E. H. Goodnow, St. Paul, Minn.	2.23 2.24	0.336 0.333	0.063 0.057	5.42 5.42	Medium immediate.

[1] All results average of two determinations.

COMMENTS OF ANALYSTS.

W. B. White: Solids.—We had no platinum dishes of proper size; so 50 mm. fused silica dishes were used. Owing to the elasticity of the term "thick sirup," the samples were heated on the water bath for exactly 1 hour, giving in this case a thick, heavy sirup. *Ash.*—The muffle used was at such a temperature that 0.5 gram of c. p. sodium chlorid lost no weight when heated one-half hour. Seven evaporations and heatings were made, but there was no loss after the first four. The ash was of a reddish cast, as usual. Have never been able to get a gray ash on vinegar.

E. H. Goodnow: No platinum dish of the proper size was available for the solids determination and, therefore, a round-bottom platinum dish of 25 cc. capacity with a diameter of approximately 70 mm. at the rim was substituted.

DISCUSSION.

While reports were received from only five of the collaborators the results in general show remarkably close agreement. Omitting Clarke's figure, the solids fall within the limits 2.23 to 2.27 grams, a difference of only 0.04 gram, although platinum dishes of the prescribed shape and diameter were not available in two instances. The ash varied from 0.325 to 0.341 gram, a difference of only 0.016 gram on nine determinations. While the variation in the results for fixed acids is somewhat larger than would be expected most of the values are fairly concordant. The volatile acid determinations, excepting the figures obtained by Miss Childs, show a range of 5.376 to 5.42 grams or less than 0.05 gram difference. The estimates of the lead precipitation are as close as the somewhat indefinite standards of grading will permit.

These methods have been generally used in the Bureau of Chemistry for the analysis of vinegars for several years but have never been submitted to collaborative test by the association with the sole exception of the method for solids. In each instance there has been either a modification of the original method as given in Bulletin 107, Revised, or a more

detailed and exact statement of the procedure. While these particular methods are among the least exacting in the analysis of vinegar, they have been submitted to coöperative test this year in order that they might be available for adoption as provisional methods and thus receive the official sanction of the association. If favorable action is taken all the methods commonly used in the examination of vinegars, with the exception of the methods for polarization and alcohol precipitate, will have been adopted as provisional methods.

RECOMMENDATIONS.

It is recommended—

(1) That Methods 6, 11 15, 16, and 17, as given in the 1911 proceedings (Bur. Chem. Bul. 152, p. 126) be adopted provisionally.

(2) That methods 10 and 20, as printed in the 1911 proceedings (Bur. Chem. Bul. 152, pp. 126–127) be given further study following the suggestions of the last associate referee, Mr. Bender, as given in Bureau of Chemistry Bulletin 162, page 81.

REPORT ON FLAVORING EXTRACTS.

By A. E. Paul (Bureau of Chemistry Food and Drug Inspection Laboratory, Chicago, Ill.), *Associate Referee.*[1]

The work this year was planned in accordance with the resolutions adopted in last year's meeting. Howard's method for oil in peppermint extract, slightly modified (using carbon bisulphid) by the associate referee, was recommended for further study with a view to its final adoption at this meeting: also that it be tried out on other flavoring extracts.

In accordance with these resolutions, eight samples were sent to the collaborators, each of the extracts containing 5 per cent of the respective oil. The extracts were anise, cassia, cinnamon, clove, nutmeg, peppermint, spearmint, and wintergreen. Collaborators were requested to apply the modified Howard method in all cases, and in addition, in certain cases, the following other methods, which have been previously recommended and appear to have considerable merit: Extraction method of Hortvet and West, as described in Bureau of Chemistry Bulletin 137, page 75, the brine modification of Mitchell's method, as devised by Hortvet and West, described in the Journal of Industrial and Engineering Chemistry, 1909, volume 1, and the saponification method for wintergreen, as described by the same authors in the same number of the same journal.

Collaborators were requested to apply the various methods not only to the extracts sent, but to dilutions representing one-half and one-fifth

[1] Read by B. G. Hartmann.

the original strength; their reports, then, are on 5 per cent, $2\frac{1}{2}$ per cent and $\frac{1}{2}$ per cent extracts in 95 per cent alcohol.

Unfortunately, the number of collaborators who have responded was very small and, still more unfortunately, two of these had had very little experience with extracts.

RESULTS OF COLLABORATION.

Analytical results on anise and nutmeg extracts.

COLLABORATOR	OIL PRESENT	OIL IN ANISE EXTRACT		OIL IN NUTMEG EXTRACT	
		Brine method	Carbon bisulphid method	Brine method	Carbon bisulphid method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
E. H. Berry.......	5.0	4.6	5.0	5.0	4.9
	2.5	2.4	2.4	2.4	2.4
	0.5	Trace	0.5	0.5	0.5
H. A. Halvorsen....	5.0	5.0	5.2	4.8	5.0
	2.5	2.4	2.7	2.4	2.4
	0.5	0.4	0.6	0.5	0.5
J. S. McCune......	5.0	4.5	4.9	5.1	4.8
	2.5	2.3	2.5	2.5	2.4
	0.5	0.3	0.5	0.4	0.6
H. B. Mead.......	5.0	4.7	4.8	4.5	2.8
	2.5	2.4	2.4	2.0	4.0
	0.5	....	....	....	1.8
Paul Rudnick.....	5.0	5.4	5.6	5.0	4.4
	2.5	2.8	2.8	2.5	2.0
	0.5	0.4	0.6	0.5	Trace

These results are interesting in showing the value of experience on certain products. The first three collaborators have done a great deal of extract work while the last two have devoted themselves more largely to other products. Of the two methods, the first is simpler, and easier of application, while the second requires a little more experience. All collaborators, therefore, obtained fair results by the brine method, but the more experienced ones, only, succeeded with the carbon bisulphid method. The results obtained by these three men are about equally satisfactory by the two methods, but it seems that preference should be given to the simpler method, namely, the brine method of Hortvet and West.

Analytical results on wintergreen extract.

COLLABORATOR	OIL PRESENT	OIL IN WINTERGREEN EXTRACT	
		Saponification method	Carbon bisulphid method
	per cent	*per cent*	*per cent*
E. H. Berry	5.0	5.0	5.0
	2.5	2.4	2.5
	0.5	0.5	0.5
H. A. Halvorsen	5.0	4.8	5.0
	2.5	2.4	2.5
	0.5	0.5	0.5
J. S. McCune	5.0	4.9	4.9
	2.5	2.4	2.5
	0.5	0.5	0.6
H. B. Mead	5.0	5.0	4.6
	2.5	2.5	2.0
	0.5	......	......
A. E. Paul	5.0	......	5.0
	2.5	......	2.5
	0.5	......	0.5
Paul Rudnick	5.0	5.0	5.2
	2.5	2.6	2.6
	0.5	0.6	0.6

In this case all collaborators obtained splendid results by both methods. Inasmuch as the methods are based on entirely different principles, one depending upon the amount of salicylic acid present, and the other upon the oil content, it would seem well to adopt both. Certainly the gravimetric process should be made official at once.

Analytical results on peppermint and spearmint extracts.

COLLABORATOR	OIL PRESENT	OIL IN PEPPERMINT EXTRACT		OIL IN SPEARMINT EXTRACT	
		Brine method	Carbon bisulphid method	Brine method	Carbon bisulphid method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
E. H. Berry	5.0	6.0	4.9	4.8	4.8
	2.5	2.6	2.5	1.8	2.4
	0.5	0.4	0.5	Trace	0.5
H. A. Halvorsen	5.0	5.7	5.1	4.2	4.8
	2.5	2.5	2.6	1.7	2.3
	0.5	Trace	0.5	0.0	0.5
J. S. McCune	5.0	5.8	5.2	4.2	4.8
	2.5	2.6	2.5	1.7	2.4
	0.5	0.5	0.5	Trace	0.5
H. B. Mead	5.0	5.5	4.3	4.1	4.0
	2.5	2.2	2.0	1.4	1.8
	0.5	......	......	......	
A. E. Paul	5.0	......	5.0	......	5.0
	2.5	......	2.5	......	2.4
	0.5	......	0.4	......	0.4
Paul Rudnick	5.0	6.0	5.0	4.6	4.2
	2.5	3.0	2.2	2.0	2.0
	0.5	0.6	0.5	0.2	0.4

The remarks made in connection with anise and nutmeg extracts apply here also. The carbon bisulphid method yields to the operators, experienced with extracts, remarkably accurate results and, it seems, should be finally adopted for these two extracts.

Analytical results on cassia, cinnamon, and clove extracts.

COLLABORATOR	OIL PRESENT	OIL IN CASSIA EXTRACT			OIL IN CINNAMON EXTRACT			OIL IN CLOVE EXTRACT		
		Brine method	Extraction method	Carbon bisulphid method	Brine method	Extraction method	Carbon bisulphid method	Brine method	Extraction meth d	Carbon bisulphid method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. H. Berry.....	5.0	5.6	4.8	4.4	3.6	4.5	4.1	5.4	4.8	5.0
	2.5	1.0	2.0	2.0	1.2	2.3	1.8	1.8	2.4	2.4
	0.5	Trace	0.5	0.5	Trace	0.3	0.5	Trace	0.5	0.5
H. A. Halvorsen	5.0	2.8	4.8	4.3	3.1	4.6	4.3	4.2	5.0	5.0
	2.5	0.5	2.4	3.1	0.9	2.3	2.1	1.2	2.6	2.5
	0.5	0.0	0.5	0.4	Trace	0.5	0.4	0.0	0.5	0.4
J. S. McCune...	5.0	3.8	4.7	4.2	4.4	4.5	4.2	3.4	3.7	4.8
	2.5	0.7	2.3	2.0	1.5	2.7	2.0	1.3	2.3	2.4
	0.5	Trace	0.5	0.4	Trace	0.5	0.4	Trace	0.5	0.5
H. E. Mead	5.0	2.6	4.7	3.9	3.2	4.1	3.9	3.8	4.9	4.0
	2.5	3.3	2.4	1.6	0.8	2.1	1.3	1.0	2.4	1.8
	0.5	0.8	0.5	......	......	..0.4	......	......	......	
Paul Rudnick...	5.0	3.6	4.6	4.4	3.6	4.5	4.1	4.4	4.4	4.4
	2.5	1.0	2.2	1.8	1.6	2.3	1.8	1.8	2.0	2.0
	0.5	Trace	1.6	0.4	Trace	0.4	Trace	Trace	0.4	0.4

In these cases the extraction method yields results which are reasonably accurate. The carbon bisulphid method, too, is very satisfactory for clove extract and may well be used as a check method but it does not appear that any change in the present status is called for as the extraction method is now official for these three products.

REMARKS BY COLLABORATORS.

E. H. Berry: The brine method seems to be entirely satisfactory for nutmeg extract and fairly so for anise. The carbon bisulphid method gave good results on anise, cloves, nutmeg, peppermint, spearmint, and wintergreen, but the results are low in cassia and cinnamon. On cassia, cinnamon, and cloves the extraction method gave good results, but there is a great deal of chance connected with the method owing to the difficulty in knowing when to stop the heating. With considerable practice good results might be obtained. The results reported were obtained after considerable practice and after rejecting a number of worthless figures. I would suggest drying the ether extract with calcium chlorid in all cases.

The saponification method for wintergreen gives excellent results and there is little choice between it and the carbon bisulphid method. The latter is a little shorter.

J. S. McCune: Cassia and clove oils were weighed without drying, making it necessary to let them stand until dry, which requires 3 hours, rendering the results

uncertain. By drying in each case, the oils may be weighed as soon as the ether has been boiled off and the dish cooled.

The carbon bisulphid method is the only one which may be used for all eight extracts and in every case shows the best results. The saponification method for wintergreen, the extraction method for cassia, cinnamon, and clove, the brine method for nutmeg, anise, and perhaps peppermint, all might be used as check methods.

H. B. Mead: My small experience with the brine method and the carbon bisulphid method probably makes this a very strenuous test for these.

ADDITIONAL RESULTS BY HOWARD AND ADAMS.

The following report of Howard and Adams was received after the other results had been compiled. Moreover, it embodies so many features which were not entered into by the other collaborators that it may hardly be incorporated with the matter previously considered. Inasmuch as it is a very complete report and quite interesting, it is added in full. As to the bearing which this report might have upon the conclusions and recommendations, the following remarks may be made:

As to a choice between the ether method and the carbon bisulphid process, Mr. Howard, with whom both essentially originate, seems to prefer the former. Attention should be directed, however, to the fact that in the case of peppermint extract his results with the ether method are considerably farther from the actual oil content than those reported by the other collaborators using the carbon bisulphid method.

In the case of cinnamon and cassia, his method, as applied by himself, seems to give fair results and it would seem that it might be worth while to study the process on these two products as compared with the now provisional extraction method. In the case of clove extract, the bisulphid method yielded to Howard, as well as to the other collaborators, results much nearer to the truth than did the ether process to Howard. If any change were made in the provisional method, it would seem that the carbon bisulphid method should be given preference, since, of the three methods, it is not only the simplest, but the most accurate.

It seems, therefore, that the report of Howard and Adams furnishes additional data for making the recommendations given.

COMMENTS BY HOWARD.

Brine method.—Of the two volumetric processes applicable to flavoring extracts—those of precipitation and extraction—the precipitation method has at least the virtue that it cannot give results in excess of the truth. In the case of certain oils, when present in tolerably large quantity, it is apparent that this method is capable of affording values but little below the actual. This is noticeably so with 5 per cent solutions of anise and nutmeg, so far as our results show. The latter oil, containing as it does, a considerable proportion of the comparatively volatile compound, pinene, there is a tendency to loss in those processes involving evaporation of a

Analytical results on flavoring extracts.[1]
(C. D. Howard and W. L. Adams.)

EXTRACT	BRINE METHOD			CARBON BISULPHID			ETHER (HOWARD)		
	10 cc.	5 cc.	1 cc.	10 cc.	5 cc.	1 cc.	10 cc.	5 cc.	1 cc.
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Anise	5.00 5.10	2.20 2.30	0.20 0.20	[2]5.40 [3]5.00	...... [3]2.70	...... [3]0.50	[4]5.10 [4]4.90 [5]5.00	[4]2.50 [4]2.54	..... [4]0.50 ......
Cassia	3.20 3.80	0.30 0.30	None None	[2]4.20 [3]5.20	...... [3]2.40	...... [3]None	[4]5.40 [4]5.10	[4]2.60	[4]0.60 ......
Cinnamon	4.40	......	......	[2]3.50 [3]4.70 [6]4.80	...... [3]2.20	...... [3]None ...	[4]5.40 [4]5.00	[4]2.60	[4]0.60 ......
Clove	4.10 2.80	1.60	Trace ...	[2]5.00 [3]5.00	...... [3]2.10	...... [3]0.20	[4]5.00 [2]6.20	[4]2.50	[4]0.50 ....
Peppermint	5.70 5.70 5.80	2.50 2 60	Trace	...	..	[2]0.40	[4]6.40 [4]6.00 [4]6.00	[4]3.00 [4]2.80	[4]0.54 ....
Nutmeg	4.80	2.40	0.20	....	......	......	[4]4.00 [4]4.20 [4]3.80 [4]4.00 [5]4.80 [5]4.40	[4]2.20 [4]2.40 .... [5]2.50	[4]0.20 .... [5]0.60 .....
Spearmint	4.70 4.00 4.00	1.80 1.40	Trace	[2]4.60 [6]4.40	[2]1.70 [6]2.30	[2]Trace	[4]4.20 [4]4.40 [5]5.10	[4]2.40 ...... [5]2.60	[4]0.30 ...... [5]0.54
Wintergreen[7]	4.20 4.30	2.10	None	[6]5.00	......	......	[4]5.10 [5]5.20	[4]2.50	[4]0.50 ......
Rose (85.5 per cent alcohol—a standard brand)	None	......	......	[2]0.20	......	......	[4]0.40 [4]0.40	....	....

[1] The percentages of oil present in all extracts except the rose were 5 per cent, 2.5 per cent and 0.5 per cent.
[2] Carbon bisulphid method exactly as directed.
[3] Carbon bisulphid method except that pump was not used at 100°C., and heating here continued but 10 to 15 seconds.
[4] Ether extraction, heating at 75°C. with 2 cc. saturated sodium chlorid solution.
[5] Ether extraction, heating at 50°C. with 2 cc. saturated sodium chlorid solution.
[6] Carbon bisulphid, heating 4 minutes at 55°C. only plus sodium chlorid.
[7] Winter green by saponification gave 4.85 per cent and 4.85 per cent.

solvent at a moderately high temperature. Spearmint oil seems to show a similar tendency. With weak extracts, however, particularly when prepared with strong alcohol, the separation is either very far from complete, or entirely negative. Were larger proportions of sample used and greater dilution practiced than is possible in the ordinary Babcock bottle, the results, as pointed out by Hortvet and by Mitchell, would undoubtedly be very much more satisfactory. Nevertheless, because of the impossibility of uniformly separating all, or nearly all of the oil present, and of the application of any really definite or constant correction, methods based upon precipitation do not at present seem to hold forth much promise, although the principle can, without doubt, be applied advantageously in certain cases.

Carbon bisulphid method.—In addition to securing complete extraction, we have involved in this the rather difficult problem of adjusting the method and temperature of evaporation with such nicety that the solvent will be completely eliminated, on the one hand, without loss of oil, on the other. The tenacity with which small amounts, not only of chloroform and bisulphid, but even of ether, are retained by the oily residue, is rather remarkable. While there can be no question that in the case of most oils used as food flavors, when present in fairly large quantity, extraction of all but unmeasurable traces can be effected by as little as 1 cc. of chloroform or carbon bisulphid, yet when the proportion is less than 1 per cent and particularly when the solvent is strong (95 per cent) alcohol—as in the 1 cc. dilution here involved—the separation is likely to be more or less incomplete. It is, of course, obvious that inasmuch as the latter circumstance would almost never be encountered in practice, this objection is not quite so vital as might at first appear. Extract of rose is, however, a case in point, the sample included in these tests containing 85 per cent of alcohol, with less than 0.5 per cent of oil. The writer trusts he may not seem lacking in a proper sense of modesty if he ventures to point out that the ether extraction method, as described below, proved to be the only one of the three volumetric procedures capable of properly working this particular case.

Objection may be raised to the provision concerning heating in a boiling water bath under diminished pressure. While this may involve no serious loss in the case of a few of the oils, there seems to be but little room for doubt that a serious loss may occur with others under this condition. In fact, our work would seem to indicate that even at 70°C., with the pump, material volatilization of oils of the character of nutmeg takes place following expulsion of the bulk of the solvent. In reality, the writer is convinced that the extended use of such high temperatures is unnecessary, although in some instances they may do no harm.

Finally, it might be well to investigate the possible objectionableness of the addition of as much as 1 cc. of strong hydrochloric acid in the case of such extracts as cassia, cinnamon and clove. In connection with earlier work along these lines, the impression was gained that such causes a tendency to low results through decomposition. On the other hand, the writer is still unconvinced as to the objectionableness of the simpler 1:2 sulphuric acid floating medium for oil of wintergreen, provided such is cautiously added to the well cooled oil separate.

Ether extraction method.—This procedure was proposed by the writer in 1911 (J. Ind. Eng. Chem., 1911, **3**: 252) as an improvement over his original chloroform method, concerning which certain criticisms had been raised. While it is believed that the present carbon bisulphid modification is capable, possibly following a little further adjustment, of affording good results in a rather large range of cases, yet the writer is convinced of the general superiority of the ether method, believing not only that it is applicable to a greater variety of extracts and oily preparations generally, but to the most exacting conditions as regards strength of alcohol and proportion of oil.

Under the present practice in this laboratory the temperature of evaporation is such that no serious loss is likely to occur in the case of turpentine and oils of similar volatility. The principle involved in the original chloroform method, that practically complete extraction can be effected by means of a very small volume of solvent. has been lately further extended in the ether process, through the elimination of the third shake out. While not quite so rapid as the bisulphid method, yet it is not a lengthy procedure. Following are the details as at present observed:

Pipette 10 cc. of extract into a 4 ounce separatory, the stem of which is cut off short at the stopcock. Add 50 cc. of cold water and, except in the cases of cinnamon,

cassia and clove, about 0.5 cc. of strong hydrochloric acid. Shake with 15 cc. of ether, draw off aqueous layer and transfer ether extract to a small-mouthed 50 cc. flask. Again shake with 10 cc. ether, reject aqueous portion, and wash the combined extracts with 10 cc. of ether-saturated water. Transfer the extract by means of a small funnel to a Babcock milk bottle graduated in tenths, and add 2 cc. of saturated salt solution. Connect stem of bottle with vacuum pump and immerse in a bath at 50°C. Holding bottle at an angle of 45°, shake continuously with a rotary motion (at first gently), until all but a small residue of ether is eliminated, which, with a good pump, will require 2 to 3 minutes only. Continue the heating for about 2 minutes beyond the point when, on removing bottle from the bath about every 15 seconds and giving contents a vigorous snap, no ether foam is observed. Remove from the pump and test completeness of ether removal by quietly immersing from 2 seconds in a boiling water bath; on the instant of removal simultaneously shake and apply a test flame. Repeat, and if not found ether-free, return to the first bath for another minute. Care should be observed not to expose the nearly ether-free oil to the temperature of boiling water for more than a very brief period, nor must the evaporation under the pump at 50° be unduly prolonged, else loss will result. Finally, cool, add salt solution and centrifuge for 1 minute.

While, using 10 cc. of sample, it has been found that one extraction only of 15 cc. ether is usually sufficient for the removal of all but unmeasurable quantities of oil when the latter is present in considerable amounts, yet the second extraction is necessary with small amounts. In order to reduce the error, it is our practice, when the proportion of oil is much less than 5 per cent, to take 20 cc. of sample in which case a third extraction with 5 cc. of ether is advisable.

With most extracts, a clear separation occurs readily, and the use of hydrochloric acid would seem of doubtful necessity. The acid was, however, found very helpful in the case of the nutmeg and spearmint, both of which extracts tended to give a persistent cloudy water-alcohol layer in the absence of such.

The addition of the 2 cc. of brine solution seems to be effective in assisting the elimination of the last traces of ether.

RECOMMENDATIONS.

In view of the above results, comments and conclusions, I would respectfully recommend—

(1) That the saponification method of Hortvet and West for wintergreen extract, as described in the Journal of Industrial and Engineering Chemistry, 1909, volume 1, and slightly modified in Bureau of Chemistry Bulletin 152, page 141, by the then associate referee, R. S. Hiltner, be adopted as provisional.

Method.—Mix 10 cc. of extract in a 100 cc. beaker with 10 cc. of potassium hydroxid solution (10 per cent). Heat on a boiling water bath until volume is reduced about one-half. Add a distinct excess of dilute hydrochloric acid, cool and extract with three portions of ether, 40 cc., 30 cc. and 20 cc., respectively. Filter the combined ether extracts through a dry filter into a weighed dish, wash with 10 cc. of ether and evaporate spontaneously. Dry over calcium chlorid in a desiccator and weigh. The weight of salicylic acid thus obtained, multiplied by 9.33, gives the per cent of oil of wintergreen by volume.

(2) That the following method, devised by Hortvet and West, and described in the Journal of Industrial and Engineering Chemistry, 1909, volume 1, number 1, be made provisional for anise and nutmeg extracts.

Method.—To 10 cc. of extract in a Babcock milk flask add 1 cc. of hydrochloric acid (1:1), then sufficient half-saturated salt solution previously heated to 60°C., to fill the flask nearly to the neck. Cork and let stand in water at 60°C. for about 15 minutes, occasionally giving the flask a twisting motion, and centrifuge for 10 minutes at about 800 revolutions per minute. Add brine till the oil rises into the neck of the bottle, and again centrifuge for 10 minutes. If the separation is not satisfactory, or the liquid is not clear, cool to about 10°C. and centrifuge for an additional 10 minutes.

(3) That the following slight modification of the Howard-Mitchell method, which was studied last year for peppermint extract, be now provisionally adopted for peppermint and spearmint extracts and also as an additional method in the case of wintergreen extract.

Method.—Pipette 10 cc. of the extract into a Babcock milk bottle, add 1 cc. of carbon bisulphid, mix thoroughly, then add 25 cc. of cold water and 1 cc. of concentrated hydrochloric acid. Close the mouth of the bottle with the thumb, and shake vigorously, whirl the bottle in a centrifuge for 6 minutes and remove all but 3 or 4 cc. of the supernatant liquid, which should be practically clear, by means of a glass tube of small bore and aspiration. Connect the stem of the bottle with a filter pump, immerse the bottle in water kept at approximately 70°C. for 3 minutes, removing from the bath every 15 minutes and shaking vigorously. Continue in the same manner for 45 seconds using a boiling water bath. Remove from the bath and shake while cooling. Disconnect from the suction and fill the bottle to the neck with saturated salt solution at room temperature, centrifuge for 2 minutes and read the volume of the separated oil from the top of the meniscus. Multiply the reading by 2 to obtain the per cent of oil by volume.

In the case of wintergreen, use as floating medium, a mixture of 1 volume of concentrated sulphuric acid and 3 volumes of saturated sodium sulphate solution.

THE RELATIONSHIP BETWEEN THE ALCOHOL-SOLUBLE SOLIDS AND ETHER-SOLUBLE SOLIDS IN STANDARD GINGER EXTRACT.

By C. W. Harrison and A. L. Sullivan (Bureau of Chemistry Food and Drug Inspection Laboratory, Boston, Mass.).[1]

During the course of the regular inspection work in connection with the enforcement of the Food and Drugs Act, it has frequently become necessary to determine the purity and strength of ginger extracts and tinctures. The high cost of alcohol leads to the attempt to put out extracts of low alcoholic content and of little flavoring strength. The following two analyses are typical of this class of extracts:

[1] Read by C. S. Brinton.

	Per cent	Per cent
Alcohol	46.95	24.30
Solids	0.60	0.79
Water-soluble solids	.....	0.77
Ether-soluble solids	0.06	None

Ginger, as is well known, differs from most spices in that water and weak alcohol extract a larger amount of solid matter from it than does 95 per cent alcohol; but these additional extractives add nothing to the value of the extract since the aromatic principles of the root, the essential oil and oleo resins are almost insoluble in dilute alcohol and water.

Street[1] has called attention to the importance of determining the alcohol-soluble solids of ginger extracts as a means of judging of their purity and strength, since he finds that practically all of the solids in high grade extracts are soluble in 95 per cent alcohol. No reference is made to the fact that this is also true regarding the solubility in ether and since some of the adulterants of ginger extracts, notably sugar, molasses, glycerin, caramel, etc., which would be more or less soluble in alcohol, would be practically insoluble in ether, it was decided to study the solubility of the solids in ether on extracts of known composition, made with weak and strong alcohol, and to compare the results obtained with the alcohol-soluble solids. It was believed that owing to the insolubility of the named adulterants of ginger extract in ether, this determination would show adulteration and low strength even better than the alcohol-soluble solids. It was our purpose also to show from the results, the relative strength of an extract.

Eleven samples of ginger root, representing three different varieties, were accordingly procured, ground, and analyzed with the following results:

TABLE 1.

Analysis of ground ginger.

NO.	VARIETY	ASH			ETHER EXTRACT			ALCOHOL EXTRACT
		Total	Water-soluble	Water-insoluble	Total	Volatile	Non-volatile	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent
1	African	5.85	3.40	2.45	8.15	1.50	6.65	5.42
2	do	4.40	2.65	1.75	7.60	1.57	6.03	5.88
3	do	5.40	3.57	1.83	7.17	1.55	5.62	5.93
4	Cochin	5.08	2.80	2.28	6.15	1.25	4.90	5.17
5	do	4.88	2.88	2.00	8.65	2.08	6.57	7.00
6	do	5.00	2.85	2.15	6.00	1.17	4.83	6.00
7	do	4.58	2.88	1.70	....	....	4.98	5.13
8	Jamaica	3.62	2.82	0.80	....	....	3.08	4.29
9	Jamaica, bleached	6.30	2.82	3.48	....	....	3.63	4.36
10	Jamaica	4.10	2.85	1.25	....	....	4.70	4.40
11	do	5.75	4.02	1.73	....	....	3.12	5.33
	Maximum	6.30	4.02	3.48	8.65	2.08	6.65	7.00
	Minimum	3.62	2.65	0.80	6.00	1.17	3.08	4.29
	Average	4.99	3.05	1.95	7.45	1.52	4.74	5.36

[1] Bur. Chem. Bul. 137, p. 76.

Two sets of extracts were then prepared from these, according to the method of the U. S. Pharmacopeia using 95 and 50 per cent alcohol; these were analyzed for alcohol, total solids, alcohol-soluble solids, ether-soluble solids and the ratio of the alcohol-soluble and ether-soluble solids to total solids calculated. The following results were obtained.

TABLE 2.

Analysis of ginger extract made with 95 per cent and 50 per cent alcohol.

NO.	VARIETY	ALCOHOL (PER CENT BY VOLUME)	SOLIDS (GRAMS PER 100 CC.)			RATIO ALCOHOL-SOLUBLE SOLIDS TO TOTAL SOLIDS	RATIO ETHER-SOLUBLE SOLIDS TO TOTAL SOLIDS
			Total	Alcohol-soluble	Ether-soluble		
95 PER CENT ALCOHOL:							
1	African	92.43	1.23	1.15	1.20	1:1.07	1:1.02
2	do	92.43	1.22	1.18	1.17	1:1.03	1:1.04
3	do	92.75	1.14	1.06	1.06	1:1.08	1:1.08
4	Cochin	91.36	1.04	1.01	0.99	1:1.03	1:1.05
5	do	91.78	1.50	1.40	1.35	1:1.07	1:1.11
6	do	92.74	1.04	1.03	0.97	1:1.01	1:1.07
7	do	92.00	1.16	1.08	1.05	1:1.07	1:1.10
8	Jamaica	92.43	0.80	0.79	0.71	1:1.01	1:1.12
9	Jamaica bleached	93.12	0.93	0.87	0.82	1:1.07	1:1.13
10	Jamaica	93.12	0.85	0.80	0.76	1:1.06	1:1.12
11	do	93.44	1.14	1.04	1.00	1:1.09	1:1.14
	Maximum	93.44	1.50	1.40	1.35	1:1.01	1:1.02
	Minimum	91.36	0.80	0.79	0.71	1:1.09	1:1.14
	Average	92.51	1.09	1.04	1.01	1:1.05	1:1.09
50 PER CENT ALCOHOL:							
1	African	49.60	1.90	0.79	0.32	1:2.41	1:5.94
2	do	49.44	1.82	0.76	0.31	1:2.39	1:5.87
3	do	49.01	2.15	0.87	0.27	1:2.47	1:7.97
4	Cochin	49.71	1.70	0.98	0.38	1:1.73	1:4.48
5	do	49.60	2.17	1.07	0.54	1:2.03	1:4.02
6	do	49.60	1.59	1.05	0.40	1:1.51	1:3.98
7	do	49.44	2.18	0.78	0.38	1:2.80	1:5.74
8	Jamacia	49.17	1.93	0.34	0.19	1:5.68	1:10.16
9	Jamaica bleached	48.00	2.15	0.35	0.29	1:6.01	1:7.41
10	Jamaica	47.17	2.17	0.31	0.24	1:7.00	1:9.04
11	do	49.33	2.47	0.59	0.37	1:4.18	1:6.68
	Maximum	49.71	2.47	1.07	0.54	1:1.51	1:3.98
	Minimum	47.17	1.59	0.31	0.19	1:7.00	1:10.16
	Average	49.09	2.02	0.72	0.34	1:3.47	1:6.48

A study of these analyses shows that in the strong extract the total solids vary from 0.8 to 1.50 grams per 100 cc., the alcohol-soluble solids from 0.79 to 1.40 grams, the ether-soluble from 0.71 to 1.35 grams, the ratio of alcohol-soluble to total solids from 1:1.01 to 1:1.09, and the ether-soluble to total solids from 1:1.02 to 1:1.14. It appears, therefore, from these results that in an extract prepared with 95 per cent alcohol, practically all of the solids are soluble in ether as well as in alcohol, and the ratio of

the ether-soluble solids to the total solids is nearly the same as the ratio of the alcohol-soluble solids to total solids, being a trifle higher.

The results on the extract prepared with 50 per cent alcohol, however, are quite different. As would be expected, the total solids are considerably higher and the solids soluble in alcohol are as a rule about 40 per cent of the total solids, with an existing ratio ranging from 1:1.51 to 1:7.00, with a general average of about 1.2:5. In the case of the ether-soluble solids, however, a much higher ratio exists since the ether-soluble solids are much lower than the alcohol-soluble solids (generally about 50 per cent) and the ratio of ether-soluble solids to total solids is found to range from 1:3.98 to 1:10.16, being generally above 1:5. It therefore appears that while the solids from a high grade extract are almost completely soluble in ether, only a very small amount of the solids from an extract prepared with weak alcohol are ether-soluble, and that, with a very dilute extract as the analysis before quoted where the alcoholic strength was 24 per cent, there were no ether-soluble solids, and such extracts are therefore practically valueless.

Ginger extracts prepared with 50 per cent alcohol have, as compared with extracts made with 95 per cent alcohol, about twice the amount of solids, 70 per cent of the amount of alcohol-soluble solids and 33 per cent of the amount of ether-soluble solids.

GINGER, NO. 6	SOLIDS SOLUBLE IN				
	Alcohol 95 per cent	Alcohol 75 per cent	Alcohol 50 per cent	Alcohol 25 per cent	Water
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Solids soluble in ether	6.00	8.92	9.20	9.82	13.39
	6.00	4.10	2.76	0.10	0.1

It is self-evident from these tabulated figures that strong alcohol must be used to get the full flavoring strength of the ginger.

The official methods were followed in the determination of alcohol, solids, and alcohol-soluble solids as given in the 1910 Proceedings (Bur. Chem. Bul. 137, p. 79). For the ether-soluble solids 10 cc. were evaporated in a porcelain dish to complete dryness. Absolute ether was then added to the residue, the dish covered with a watch glass and allowed to stand 15 minutes. This ether was then decanted through a dry filter into a tared 100 cc. Erlenmeyer flask, and the ether washing repeated. The undissolved solids remaining in the dish were then scraped loose from the sides with a spatula and rubbed up with successive small portions of ether which were passed through the filter until no more material was dissolved, as indicated by the ether coming through colorless. The ether was then distilled off and the flask dried at 100°C. to constant weight.

SUMMARY.

From the analytical results the following conclusions are drawn: The solids in ginger extracts made with 95 per cent alcohol are practically all soluble in ether, this being true of all three varieties examined. Only a small amount of the solids from ginger extract made from weaker alcohol is soluble in ether, and the solubility of the solids in ether decreases the weaker the alcoholic extract, even though the amount of total solids increases, and in the case of the 25 per cent extract, practically none of the solids were soluble in ether.

The solids from extracts made with weak alcohol are more insoluble in ether than in alcohol. Some of the adulterants of ginger extracts, as molasses, caramel, glycerin, sugar, etc., would be more insoluble in ether than in alcohol, and, therefore, the percentage of solids soluble in ether conveys more information as to the strength of a commercial ginger extract than the amount of alcohol-soluble solids.

The amount of ether-soluble solids in connection with alcohol-soluble solids is a valuable measure of the strength of the extract.

REPORT ON SPICES.

By R. W. Hilts (Bureau of Chemistry Food and Drug Inspection Laboratory, San Francisco, Cal.), *Associate Referee.*

At the 1913 meeting of the association, there were referred to the associate referee on spices, the recommendations of the associate referee on condiments other than spices for 1911, as the refereeship on condiments other than spices was dropped in 1912. These recommendations concerned in particular the examination of tomato ketchup with special reference to the detection of spoilage, and the work was continued in 1912 when the methods for the determination of lactic acid, citric acid, insoluble solids, and sand were approved for final action as provisional in the following year. The present associate referee has had no opportunity to make a special study of the methods, but would state that the methods for citric acid, lactic acid, and insoluble solids (Bur. Chem. Bul. 162, pp. 128–129) are used in the San Francisco laboratory of the Bureau of Chemistry, as occasion arises, for the examination of ketchup. While the lactic and citric acid methods appear to have a value in detecting the use of decomposed pulp, this value is only as confirmatory of the microscopical methods, which must still be the main reliance. The lactic acid method is laborious, and, in a mixture such as ketchup, must be regarded as merely conventional, and its results must be taken as relative and not as absolute.

With the idea of finding some method that might yield lower "blank" results on ketchup, a few preliminary experiments were made to test the availability of the method of Möslinger,[1] which depends upon the solubility of barium lactate in 70 per cent alcohol. At present it appears probable that the complications caused by the presence of sodium benzoate might make the method quite cumbersome, even if applicable.

Certain facts deserve consideration: The lactic acid method which has been under study is laborious and its results, as well as those of the citric acid method, are relative. Research work on the determination of lactic and other organic acids is under way in the Bureau of Chemistry. The lactic and citric acid methods have received the approval of the Secretary of Agriculture for official use, so that immediate adoption is not necessary.

It is recommended that final action regarding the lactic and citric acid methods be withheld pending further study and collection of data and that the methods for determining insoluble solids and sand, as applied to ketchup (Bur. Chem. Bul. 162, pp. 128–129), be adopted as provisional.

REPORT ON BAKING POWDER.

By Roe E. Remington (Agricultural Experiment Station, Agricultural College, N. D.), *Associate Referee.*

Early in the year the associate referee sent out about fifty copies of a circular letter suggesting four determinations for study on baking powders. From replies received, it seemed that the question of lead was of most interest, and after some correspondence with the associate referee on heavy metals it was decided to take up the study of this determination in baking powders, particularly those of the alum-phosphate type.

Correspondence with a number of chemists and a study of last year's report on lead, led to the conclusion that our present methods are not sufficiently perfected for collaborative work on samples. Accordingly, this year's study has taken the direction of attempts to simplify and improve existing methods to the point where they may be placed in the hands of a number of chemists for check determinations.

The associate referee has had the coöperation of several chemists in this study, and begs to submit the following modification of existing methods as a result of the year's work. He would recommend for next year that a comparative study be made of the Seeker, Exner and referee's methods for this determination. The latter is as follows:

[1] Zts. Nahr. Genussm., 1901, **4**: 1120; 1914, **27**: 841.

REFEREE'S MODIFICATION OF SEEKER METHOD.

Weigh 100 grams of baking powder into an 800 cc. Jena beaker and add 75 cc. of hydrochloric acid in small portions, with stirring, followed by 200 cc. of distilled water. Place the mixture on a steam bath and heat until the starch is completely hydrolyzed and the solution is fairly clear and a bright yellow. (Too long heating will result in darkening due to caramelization. A copious crystalline precipitate of calcium phosphate may appear, but will do no harm.)

Neutralize the solution to the point of precipitation of aluminum with ammonia, cool, and add 400 cc. of a 20 per cent ammonium citrate solution saturated with hydro gen sulphid.

This citrate solution is prepared as follows: Prepare a solution containing 200 grams of ammonium citrate per liter in a bottle fitted with a two-hole stopper. Through one hole, make connection with a generator producing hydrogen sulphid, and to the other attach a siphon for drawing off the solution. The liquid is thus kept saturated with hydrogen sulphid, and at the same time may be drawn off without disturbing the precipitate of lead sulphid which has gathered on the bottom. Practically all the ammonium citrate on the market contains lead. By preparing the solution as just described the loss due to solubility of lead sulphid is reduced to a minimum, the reagent being already saturated with this salt.

The baking powder solution will be slightly alkaline, so that a partial precipitation of iron sulphid will result, together with that of the lead. Allow the solution to stand covered, passing in more hydrogen sulphid if the odor of the gas disappears, until the precipitated sulphids settle. Siphon or filter off the supernatant liquid, collect the precipitate on a filter and wash with a small amount of hydrogen sulphid water. Then place the filter with the precipitate in a tall 100 cc. Jena beaker, add 5 cc. of sulphuric acid and 10 cc. of nitric acid, and heat on the hot plate with occasional additions of nitric acid until the solution is colorless and all organic matter is destroyed. The solution will contain a precipitate of calcium sulphate. Continue the heating until a large portion of the sulphuric acid has passed off, but not to dryness. Cool, add 5 cc. of water and heat gently to aid solution. Again cool, neutralize with ammonia, and add 30 cc. of a mixture of equal parts of saturated lead-free ammonium acetate solution and 96 per cent alcohol. Allow to stand overnight, filter and wash with a small amount of ammonium acetate alcohol solution. If the precipitate of calcium and ammonium sulphates is heavy, it may be necessary to use suction.

Acidify the filtrate with acetic acid and heat nearly to boiling. Precipitate with potassium dichromate solution, allow to stand overnight, filter on a small tared Gooch, wash with a small amount of cold water, dry at 125° C. and weigh as lead chromate.

No report was made by the associate referee on meat and fish.

REPORT ON FATS AND OILS.

By R. H. Kerr (Bureau of Animal Industry, Washington, D. C.), *Associate Referee.*

The 1914 work consisted of a study of methods for the detection of phytosterol in mixtures of animal and vegetable fats. Two methods were studied, the one developed in the laboratories of the Bureau of Animal Industry and the digitonin method of Marcusson and Schilling.

Three samples were sent out for the work, the composition of them being as follows:

Sample 1—Lard adulterated with 5 per cent of cottonseed oil and 0.25 per cent of vaseline.

Sample 2—Pure lard (rancid).

Sample 3—Lard adulterated with 2.5 per cent of hydrogenated cottonseed oil and 2.5 per cent of soy bean oil.

Vaseline was added to Sample 1 in order that the effect of its presence on the methods studied might be determined. Such an amount of vaseline would effectually prevent the obtaining of any accurate results by the present provisional method. A rancid lard was chosen for Sample 2, for similar reasons. Rancidity interferes decidedly with the present provisional method.

The following instructions were sent to the collaborators:

INSTRUCTIONS TO COLLABORATORS.

The work consists of a study of methods for the phytosterol acetate test. Three samples of fats for this work are being sent you under separate cover. You are requested to test these samples for phytosterol according to the methods given below.

1. Bureau of Animal Industry method.—Described in Bureau of Animal Industry Circular 212, a copy of which is being sent you herewith.

2. Digitonin method of Marcusson and Schilling.—(Chemiker Zeitung, August 21, 1913.) Shake vigorously for 15 minutes in a separatory funnel 50 grams of the fat oil or fat to be tested with 20 cc. of a 1 per cent solution of digitonin in 95 per cent alcohol. Allow the mixture to stand for a time until the emulsion separates. The lower or fat layer should be quite clear while the alcohol layer is full of a bulky, flocculent precipitate. Draw off the fat as much as possible, taking care not to lose any of the precipitate. Add 100 cc. of ether to the alcohol layer and filter the mixture. Wash the precipitate with ether until free from fat; after drying in the air, transfer it to a tall 50 cc. beaker, add 2 to 3 cc. of acetic anhydrid and cover the beaker with a watch glass. Then boil slowly over a low flame for half an hour. After cooling, add 30 to 35 cc. of 60 per cent alcohol and thoroughly mix the contents of the beaker. Filter off the alcohol solution and wash the precipitate with 60 per cent alcohol, then dissolve it on the filter with a stream of hot 80 per cent alcohol from a wash bottle and set away the filtrate in a cool place (10° C. or below). After the acetates have crystallized out of this solution filter them off, recrystallize from absolute alcohol, dry, and determine the melting point as directed in Bureau of Animal Industry Circular 212.

You are requested to test the three samples sent you for phytosterol by both methods and to report (1) melting point of acetates obtained in first crystallization from absolute alcohol, (2) melting point of each subsequent crop of crystals, if acetates are recrystallized, (3) judgment as to presence of vegetable oil, and (4) which of the two methods you consider preferable. Any comment or suggestion you may care to make will be appreciated.

RESULTS OF COLLABORATORS.

Results by L. B. Burnett (Bureau of Chemistry).

Sample	*Melting points by B. A. I. method*	*Melting points by Digitonin method*	*Conclusion*
1	114.8°—1st crop crystals 115.6°—2d crop crystals	114.8°—1st crop crystals 116.0°—1st crop crystals 115.8°—1st crop crystals	Phytosterol present
2	111.8°—1st crop crystals 112.0°—2d crop crystals	111.4°—1st crop crystals 112.2°—1st crop crystals	No phytosterol present
3	115.8°—1st crop crystals 116.4°—2d crop crystals	116.0°—1st crop crystals 116.6°—1st crop crystals	Phytosterol present

Mr. Burnett expresses a preference for the digitonin method over the B. A. I. method and recommends using a 100 gram sample for the test.

Results by R. S. Hollingshead (Bureau of Chemistry).

Sample	*Melting points by Digitonin method*	*Conclusion*
1	116.5°—1st crop crystals 116.1°—2d crop crystals	Vegetable oil present
2	114.2°—1st crop crystals 113.6°—2d crop crystals	Pure lard
3	115.8°—1st crop crystals 115.4°—2d crop crystals	Vegetable oil present

Mr. Hollingshead reports no results by the B. A. I. method. He expresses a preference for the digitonin method on the ground of convenience.

Results by R. H. Kerr (Bureau of Animal Industry).

Sample	*Melting points by B. A. I. method*	*Melting points by Digitonin method*	*Conclusion*
1	115.4°—1st crop crystals 116.2°—2d crop crystals	117.4°—1st crop crystals	Vegetable oil present
2	113.6°—1st crop crystals 114.0°—2d crop crystals	114.4°—1st crop crystals	No vegetable oil
3	117.0°—1st crop crystals	117.6°—1st crop crystals	Vegetable oil present

These results show no choice between the two methods with regard to accuracy. Each method led to uniformly correct conclusions. Choice between the two methods must then depend on other factors. The digitonin method offers the advantage of simplicity and convenience and has the disadvantage of demanding an expensive reagent, which also is limited in supply, and obtainable only with difficulty. The B. A. I. method lacks this disadvantage, but requires more time and labor for its manipulation. Both methods are decidedly superior to the present provisional method.

RECOMMENDATIONS.

It is recommended—

(1) That the B. A. I. method for the detection of phytosterol in fats (B. A. I. Cir. 212), be adopted as a provisional method.

(2) That the digitonin method as described in this report be also adopted as a provisional method.

(3) That the glycerin saponification method for the preparation of fatty acids for use in the titer test (Bur. Chem. Cir. 108, p. 11) adopted last year as a provisional method, be made official.

(4) That Emery's method for the detection of beef fat and other solid fats in lard (B. A. I. Cir. 132) adopted last year as a provisional method, be made official.

PRESIDENT'S ADDRESS.

By E. F. Ladd (Agricultural Experiment Station, Agricultural College, N. D.).

Members of the association of official agricultural chemists: For the thirty-first time we, as members of this association, are gathered together to carry forward the work started by that little group of chemists who organized the association nearly a third of a century ago. Even though possessed of prophetic vision, little could they have realized the great benefits that would grow out from their modest beginnings, and the vast amount that would be accomplished in promoting agricultural chemistry in this country, or, how far-reaching would be the influence of the work of this association. The methods that have been developed and approved during these years have not only come to be generally recognized as official in American work and so accepted by the courts, but they are generally known and used in European countries. And yet, there remains before the association a great field, rich for the harvest, and chemists are anxiously awaiting the information.

The regulatory work demanding the attention of the chemists coming through the enactment of new laws, has made a demand for more exact analytical methods in many fields of activity. Where we had formerly fertilizer laws, then feeding stuffs laws, we now have food laws, drug laws, insecticide and fungicide laws, sanitary laws, and moving rapidly towards us, is the perplexing work with paints, varnishes, textile fabrics and scores of other products that the official chemist must be prepared to handle. In many of these fields we shall need to call for aid upon the physical chemist, the biological chemist, the microchemist, the toxicologist, the physiologist, the bacteriologist, in fact, upon the whole realm of science to bring to bear their skill and knowledge in solving the problems of the people and to hold the prestige that is ours as workers in this great field now spread out before us.

The splendid work which has been done in the past and the commanding position for our association and its workers has been made possible by the generous aid of the Bureau of Chemistry in all of our undertakings, and, to a great degree, by the publication by the Secretary of Agriculture, of our past proceedings as well as of the methods of analysis, as now given in Bulletin 107, Revised. Our work can never end for each year presents us new problems to be solved, new investigations to be undertaken, new lines of research to be developed, which call for new and improved methods of analysis in the great field of agriculture as well as in the official regulatory work for protecting the public health and in the prevention of fraud and deception. The work of this association has gained a place because the information resulting from these gatherings has been placed in an available form before the public for the use of our chemists. It is most unfortunate, therefore, that the Department of Agriculture has, by legal restrictions, been unable to continue the publishing of these important proceedings and, especially so, since the methods approved by the association, are now generally recognized as official under both State and Federal regulatory laws and, at a time, when we, as official chemists, need all the chemical information possible to be secured to aid us in preparing for our official duties.

DISCUSSION OF PUBLICATION.

As you are aware, the proceedings for the past year have not been published for lack of funds, and, since satisfactory arrangements therefore have not been perfected with any of the large publishing houses, it is vitally important that some means be found for a prompt publishing of the work of the association if we would continue to make progress, as is most essential at this time.

A series of questions were sent out to a number of chemists to get their viewpoint, and the three questions propounded on this point were:

1. How shall the proceedings of our association be published and made available for the general use of chemists?
2. Should the association attempt to publish a journal to include the proceedings and methods of analysis?
3. If an association journal be published should it attempt to care for other than official matters of the association, or should it include articles of interest to members of the association, including editorial matter of general interest?

Fifty letters were sent out, to which there have been twenty-five replies. I can only in general terms analyze the statements made by the several writers without giving due credit to the authors in each instance. Five only were strongly in favor of publishing a journal. Twelve believed the association should publish an annual report of its proceedings. It is thus observed that but few are favorable to publishing a journal, chiefly on

the ground of expense, and, for the further reason, that there are already a large number of chemical journals available. It should be borne in mind, however, that there is no definite publication devoting its attention to the particular field of work which this association represents. Several of the chemists were strongly in favor of again urging the Department of Agriculture to publish the proceedings, as in the past, since the work is largely of an official character and must be the basis for analytical work in connection with the enforcement of food and drug laws, both State and Federal.

On the other hand, there are those who are equally strong in favor of the publication of a journal quarterly to include the proceedings of the association and admit that there are many financial difficulties in the establishment and maintenance of a new journal, but believe that the labors of the agricultural chemists will justify the establishment of such a journal.

Mr. Frear stated:

> The Association of Official Agricultural Chemists is probably the most broadly representative organization comprising the interests of agricultural chemists. Considering the volume of its present labors, I should not think it wise to enlarge the scope or program of its meeting, but I do not see why that should limit the scope of its journal to purely official subjects. As a matter of strategy, I would suggest that the proceedings of the association appear in sections, separately paged, and added as a supplement to the journal, and that the proceedings be distributed through the numbers of the journal in such a way as to promote its circulation among the various laboratories of the country, whose chemists need to keep acquainted with the changes in official methods and the reasons therefor. A separate pagination in this way would permit of its binding into a separate volume.

Mr. Fraps stated:

> The proceedings should be published either as a single publication or in periodical issues. It does not appear to me that the subject matter lends itself readily to periodical treatment, but would better appear as a single publication.

Mr. Alsberg, who has been acting for the committee appointed at the last association meeting, to examine into the matter of publishing the proceedings, stated:

> On the whole it seems to me that the reports have not been very encouraging. Personally, I feel that the journal could serve a valuable purpose in two ways: First—by printing a lot of material in the way of data and analyses which are unavailable to food, drug and feed control officials, and which are more in the nature of statistics and, therefore, not available for publication in ordinary research journals; second—by the stimulus it will give to scientific research.

Analyzing the data as gathered thus far by Mr. Alsberg, it would appear that there are 98 subscriptions promised and 20 probable subscriptions,

or, a total of 118 subscriptions. This is hardly a sufficient guarantee to warrant one in proceeding with the publication of the journal. The matter is, therefore, at this time placed squarely before the association as to what steps shall be taken with regard to the publication of the proceedings of this association. Shall the association attempt the publication of its proceedings in pamphlet form, to be furnished to the members of the association, and sold to those interested in the work, or, shall the association take steps looking toward the publication of a journal or periodical, say quarterly, and thus be able to avail itself of the postal rates, at the same time furnishing a medium for the publication of a vast amount of information of great importance to the agricultural and food chemists, and in this way stimulating research work in agricultural and food chemistry? For example, like the *Analyst* of London for the food work and supplements each quarter to contain the proceedings and revised methods of analysis, or, after the fashion of the *Zeitschrift für Analytische Chemie*. In either case, how can we finance this undertaking so as to ensure success?

As an association we can not afford to neglect publishing our proceedings, but it does seem to me that we may well edit out a portion of the material in the published proceedings and summarize more fully the data.

Many think too much time is given to hearing the reports of the referees, and not enough to the discussion of results, or to the methods which are proposed for the use of the association.

Professor Christensen of New Mexico thinks it would be far better, instead of publishing a new journal, to try to affiliate with the American Chemical Society in such a way that some one of the journals of that society would create a section on agricultural chemistry to be devoted to articles bearing on the various phases of agricultural chemistry and such other matters as may be of special interest to the Association of Official Agricultural Chemists.

Undoubtedly, the secretary will be able to present to you some further information with regard to the possibilities of publishing the proceedings of this association.

REFEREE AND COLLABORATIVE WORK.

With the vast number of research problems confronting the members of this association, the question is raised as to how we shall secure the best possible results in a reasonable length of time. There are those who have thought that some improvement might be made in handling the vast amount of work now in the hands of the referees. Some have felt that too much time, at the association meetings, is taken up in the presentation of formal reports and the immense amount of detailed analytical data quite impossible for the hearer to follow; that not enough time is given to

the discussion of important matters before the association. If this be true, how we shall remedy it is a perplexing question, and it is my purpose to point out some of the opinions expressed by our members in order that the matter may be brought more directly to your attention; trusting, in this way, that we may be able to find a remedy.

None seem to think it desirable to discontinue our present methods, especially, the sending out of samples to try out methods, but the chief point seems to be that too large a field of work is assigned and that by restricting the work to a narrower field or to a single problem, more could be accomplished. Again, not enough interest is taken in many of the laboratories, my own included, to accomplish what should be done in collaborative work. The least experienced, in reality, apprentices, too often are entrusted with the analytical work of trying out the methods because our laboratories are overcrowded and so render it practically impossible for the better trained men to do work of this kind. So the work is slow and, at times, possibly methods have been condemned because there has not been a fair try-out by well trained chemists. Can we not accomplish more by having two types of work? Let chemists be appointed individually, or in group committees of three, as may seem most desirable, chemists who are known to be interested in certain fields, to take up the necessary research questions and to develop methods; and, when this much has been accomplished, turn the matter over to the referees that the methods may be tried out by a few select workers in the same field before the testing-out process begins by sending out samples. By this method it seems to me that a half-dozen research problems could be attacked by different workers, where we now have only one. Methods could be developed which would be far more satisfactory and the work done much more rapidly than by the present system. Let us not, however, lose any of the essential benefits arising from the splendid line we have already developed. As illustrating the views of different chemists, I quote from their statements. One stated:

The only criticism I can make of the work of the referees is that they have in many cases been assigned a great subject which involved a lifetime work, or, at any rate, work for many years to cover it completely. It would be a big improvement in my opinion if, instead of assigning general subjects, little portions of that subject be assigned by the Executive Committee, according to a definite plan, so that only one small investigation at a time is occupying the referee. Then the whole subject will be gradually covered by the referee, or a series of referees, in the course of a few years.

A subject like feed adulteration, for instance, in general terms, without any specific problem involved, does not seem a profitable way to get any clean-cut results. More, I think, could be accomplished by selecting one or two definite forms of adulteration and instructing the referee to work and report on that instead of letting him wrestle with the whole subject.

I feel very strongly that the referee should be given the greatest amount of freedom in the handling of his subject. I also feel, however, that in outlining his work he should only plan for as much as he feels he will be able to complete during his two years as referee. Then, if it is the feeling of the association that he has rendered very valuable service, he might be reappointed to continue the work. I think, however, that this latter course is only advisable in unusual cases.

The question of sending out samples is largely dependent, it seems to me, upon the work in hand. In many cases it will doubtless be necessary for the referee to devote his entire time to research. Again, he may have his methods worked out after a few months to such a point that he feels the need of coöperation and confirmation of his own results. In such a case I think too much emphasis cannot be laid upon sending out samples. I do feel, however, that the samples should not be sent out until after the referee has done a great deal of research and worked on the method for a sufficient time to have a very definite opinion in his own mind as to the practicability of the method. I feel that this is necessary owing to the fact that the referee, after working with a method for a long time, often becomes so familiar with it that in his hands it gives very satisfactory results, whereas, in another's hands, it may not prove satisfactory.

Another, connected with one of the leading experiment stations stated:

It has never seemed to me that the present method of trying out analytical methods has amounted to much. Progress in analytical chemistry has come from the specific and individual interest of a chemist in a given research and for which it has been necessary to develop the best methods possible. The present method fails to bring out the critical attitude of the analyst, but merely blindly follows printed directions. If assignments could be made to those individuals particularly interested in the method under investigation, then, I am sure, very much would be accomplished.

Another stated:

In the development of new methods investigation is necessary, but in the testing of methods proposed for adoption, the collective testing of methods is necessary. The system of sending out samples is to a certain extent overdone, as sometimes methods are sent out which have not been tested sufficiently by the referee himself.

Another station chemist stated:

It is our belief that assignments by a referee of work to a laboratory which has become known because of its special attention to that subject, would lead to better results than by the present system. It is our belief that in a great many cases poor results are secured by the use of a good method because of the inexperience of the worker.

Another Western chemist stated:

I think the assignment of subjects for investigation to individuals might be productive of a higher grade of work, also new and better methods.

An Eastern chemist stated:

I like the present system of sending out samples by the referees to try out methods, but think that the methods should be thoroughly tried out by the referee before sending out his samples. The trouble with this method seems to be that much of the work is now being done by the younger and more inexperienced chemists, making the matter rather a trial of men than methods.

Another:

For improvement in the work of the association, my suggestion would be to select some subjects and assign them either to committees or to individuals. We have already made a beginning in this direction in the matter of methods for basic slag. I feel that we should make further progress along this line, at the same time, continue to study methods thoroughly by sending out samples before undertaking to adopt the methods proposed.

Another:

It has seemed to me that too much time was taken up with reports on analytical methods with its tiresome array of figures, and not enough upon some new phases of agricultural chemistry, possibly even outside of analytical work. In other words, not enough time is set aside for the presentation and discussion of papers dealing with new investigations in our field.

The general tenor of the statements from the other chemists is similar to those already presented and indicate that there is a belief that at this time we can make progress more rapidly by inducing chemists who are interested in some special field of work to take up some individual problem and develop methods satisfactory therefor; and then, possibly, these methods be turned over to the referees who will proceed to try them out after they have been carefully tried out by associate chemists interested in the same field of work.

I would also call your attention to the desirability of increasing the membership of the Association of Official Agricultural Chemists. And in this connection would it not be desirable to admit to membership chemists representing municipal organizations, who work along the same line as that of our association? I am informed that the secretary has had several requests for membership in the association by official municipal chemists, yet, according to our Constitution, these men are not entitled to admission. Should the Constitution be amended so as to admit to membership chemists who are engaged in municipal work?

Other suggestions have been made as to how to improve the efficiency of the association, and among these suggestions is one that the referees take up too much time of the association in submitting their reports. Should the report of the referee be restricted, say, to 15 minutes? If this be done only an abstract of most reports would be presented to the

association, and in this event the Committee on Recommendations would have to go over the whole report in more detail than they do at the present time, thus, throwing more work on the committee, but it is the belief of a number of the members that such would tend to make the meetings more interesting and allow of a fuller discussion of subjects before the association.

It has been suggested also that a committee be appointed to go over very carefully the official methods of analysis as now published and include among the revised methods only those which have been actually demonstrated to be of value and dependable.

One chemist with regard to recommendations made the statement:

> I think it is about time to get some method for determining available phosphoric acid in fertilizers which makes use of a more dependable reagent than so-called neutral ammonium citrate. I think it would be well to take up and push rapidly some work along this line. Perhaps, try out some of the methods proposed by the fertilizer section of the American Chemical Society.

The general tenor of a number of the replies is that the methods and important data of the convention are not gotten out as early as they should be and made available for the use of official chemists. This improvement could best come through the publication of an official journal by the association. If a quarterly journal could be published under the auspices of the association, I feel confident much good would result and a greater stimulus would be given agricultural chemistry, such as has never been known in this country. Our workers would be more closely welded together and the benefits would be far-reaching. If, too, the Chemical Section of the National Association of Dairy, Food and Drug Officials could be induced to coöperate with us and use one issue for the proceedings of their section, it would, in my judgment, be a most desirable aid to our official work. Some method must needs be devised for publishing the proceedings if we would continue to make growth, and I strongly urge upon all our members to consider carefully at this time the best method to handle this important matter.

RECOMMENDATIONS.

As suggestions for the consideration of the association and for the betterment of the work in order to enable us to accomplish the greatest amount of good and to insure the fullest value in our undertakings I recommend—

(1) That there be appointed a committee of four or five members who are familiar with the work of the association and the problems confronting them for the purpose of receiving suggestions from members of the association with regard to problems to be solved and that the said committee canvass carefully the suggestions made, formulating there-

from plans for the future work of the association, determining what particular problems are best taken up and find possible chemists interested in this particular field of work and assign to them such phases of the work as may be carried out in a reasonable period of time, keeping in mind a definite policy for the development of the work. This committee might well be composed of one man fully familiar with soils and agriculture problems, another with fertilizer problems and another member to be familiar with the questions involved in food and drug work.

(2) That the association take action at this meeting looking to the publication of the proceedings and it seems to me after canvassing the situation carefully that a quarterly will afford us the best means of placing before the chemists the work of the association and enable us to take advantage at the same time of lower postal rates.

(3) That a time limit of 15 minutes be placed upon the papers and reports and that members be urged to condense as fully as possible the material that is necessary to report leaving the great mass of figures to the consideration of the committee or referee.

(4) That the time has come when the work might well be divided for one half day and two section meetings held, one dealing strictly with agricultural problems and the other with food and drug work. In this way the two sets of chemists would be permitted to select such meeting as they deem most nearly fitting their particular line of work; all other papers and discussions would then be presented in the full session. This would shorten the period of the meeting and permit discussion on the part of members.

(5) That there should be introduced more material which deals with problems, short papers or addresses that would be of general interest to all the members and that the time has come when our work should not be confined so exclusively to detailed methods of analysis but that there should be added constructive suggestions to encourage and stimulate investigation on the part of our younger members.

REPORT ON PROPOSED JOURNAL OF AGRICULTURAL CHEMISTRY.

By C. L. Alsberg (Bureau of Chemistry, Washington, D.C.), *Secretary.*

After giving much time and thought to the matter of publishing the proceedings of the association, and consulting with many members of the association and with various printers, I have reached the conclusion that, considering the high standing of the firm, and its great experience in publishing research journals, the proposition submitted by the Waverly Press of Baltimore, is a very fair one and the best we can secure. Unfortunately, few publishers are ready to assume even so great a risk as this.

This firm promises to publish a quarterly journal to be known as the *Journal of Agricultural Chemistry*, to be restricted to agricultural, food, and drug chemistry, to contain not less than 600 pages per volume of 4 issues; to print, bind, publish, issue, mail and distribute same; to edit manuscript; pay all expenses; solicit subscriptions and advertisements, but not to pay anything to authors for manuscript and copy for illustrations; to submit all matter to the managing editor for approval before incorporation in the journal; and to submit a make-up copy to said editor before publication. This journal is to be in all respects like the *Journal of Biological Chemistry*, published by the Waverly Press.

The association, on the other hand, must agree to the use of its name in every legitimate way in the solicitation of subscriptions and advertisements; to furnish a list of possible subscribers and to use all reasonable efforts to further the interests of said journal.

The subscription price is to be $5.00 payable in advance, but members may subscribe at $4.00. The publishers are to collect and receive all money for subscriptions and advertising and keep a list of subscribers, their records to be accessible at all times to the association. At the end of every twelve months, an account is to be rendered to the association. They are to be repaid, if sufficient funds are available, for all disbursements and expenses, and interest on money advanced, plus profit equal to 10 per cent net profit over and above all costs of material, labor, etc. They shall also receive a profit of 10 per cent on gross receipts. The 10 per cent publisher's profits, however, are not be be paid until such time as the income of the journal warrants. The association, in turn, is to receive an amount equal to the publisher's profit, and any remainder shall be equally divided. The association guarantees to pay any deficit up to $1,000.00 during any period of twelve months with the understanding that all advertising is to be credited to cost of printing the journal.

This agreement is to be binding for five years, with privilege of renewal at expiration of such time.

In case any of you are unfamiliar with the work of these publishers, I would refer you to the *Journal of the Washington Academy of Sciences*, the *Journal of Biological Chemistry*, the *Journal of Pharmacology and Experimental Therapeutics*, and the *Journal of Phytopathology*, published by this firm, all of which, as you doubtless know, have given splendid satisfaction.

The publishers feel that the publication would be more attractive if it appeared in journal form, and more so, if it included the official methods which in the past have been issued in bulletin form from time to time by the Department of Agriculture. This has the advantage to the chemist of getting such official methods before the public as soon as they are adopted, instead of waiting for periodical revisions of Department publications.

The data contained in Bulletin 107, Revised, of the Bureau of Chemistry could be published either as a part of the journal or as a supplement, and the recommendations and reports of referees could be issued as they are received. In this connection, of course, the question as to whether or not the Secretary of Agriculture would be willing to relinquish the publication of official methods would have to be presented to him for final settlement.

I feel that the question of getting advertising matter should be very seriously considered. If it is deemed advisable to secure advertisements, they would, of course, have to come under the strict censorship of the committee in charge of such journal or the managing editor. The publishers pointed out very justly, it seems to me, that as an advertising medium for dealers in apparatus and glassware, publishers of books, manufacturers of chemicals, various types of farm implements, apparatus and machinery, this journal would have considerable advertising value. Inasmuch as all proceeds from such advertisements are to be credited to the journal printing account, the number of subscriptions necessary would be correspondingly decreased, and this is a matter well worth careful thought.

It is estimated that $3,000.00 a year will be required to finance the journal, which would mean 600 subscriptions at $5.00 each, or 750 subscriptions at $4.00 each, provided it is thought best not to include advertising matter. It is also necessary that a fund be raised as a guaranty, as the subscriptions during the first year or two will probably not be sufficient to defray the entire cost of the publication.

The responses received to the circular letter sent out under date of June 15, 1914, asking for subscriptions to the journal, and contributions to the guaranty fund, have not been as promising as was anticipated. A number of members of the association have written stating that they feel there are already too many scientific journals, and that it would be inadvisable to publish a journal for this association; also that the subscription price is a little excessive. Still others have suggested that the journal be published by the American Chemical Society, and the official methods be published by the Department of Agriculture, as has been the custom in the past. Another suggestion is that in place of calling the publication the "Journal of Agricultural Chemistry," it be known as the "Journal of Official Chemists," thus giving it an official status. It has also been suggested that in place of having the annual dues $2.00, they be increased to $10.00 which would include subscription to the journal. In this way the institution would pay for the dues as well as the journal, and it would not fall so heavily upon the individuals, as might be the case if the dues remain as they are at present and a separate subscription price were assessed for the journal. Still others feel that the dues should be entirely dispensed with or materially decreased.

The following is a brief statement of the financial status of the journal at the present time.

Subscriptions promised	98	
Probable subscriptions promised	20	
Checks in payment of subscriptions, total		$60.00
Cash on hand toward guaranty fund		114.00
Amount promised toward guaranty fund		205.00
Total cash on hand		$174.00

In addition to this there have been a number of letters from members stating that they will give financial assistance in the way of launching the journal, and others have written that they will do their utmost to secure additional subscriptions. Personally, I feel that when once the journal appears, the demand for it will be very much greater than the figures just read would indicate. I am of the opinion that we would have no difficulty in finding ten men who would put up one hundred dollars a year for five years, if need be. A detailed statement has been prepared giving the names of the individuals or organizations who have promised to contribute to this project, and should any one desire to consult this list it will be found at the registration desk.

It is my personal opinion as secretary that such a journal would probably very soon be self-supporting, because it would contain very much material which would be necessary to professional and commercial chemists, as well as to agricultural, food, and drug chemists, and feed control officials, and I personally am under the impression that five or six hundred subscriptions could be easily secured even in the event that we do not include advertising matter.

The discussion of the proposed Journal of Agricultural Chemistry was postponed until the afternoon session and the meeting adjourned at 12.40 to reconvene at 2 p.m.

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PROCEEDINGS OF THE THIRTY-FIRST ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1914.

SECOND DAY.

TUESDAY—AFTERNOON SESSION.

At the opening of the afternoon session the committee appointed to call on the Secretary of Agriculture reported that he was unusually busy and regretted that he could not accept the invitation to speak to the association.

DISCUSSION OF THE PROPOSED JOURNAL OF AGRICULTURAL CHEMISTRY.

ALSBERG: The journal should give precedence to the proceedings. When the proceedings are out changes in official methods should follow immediately, and if there is any further space available it should be for the publication of such scientific papers as might be submitted.

FREAR: I feel quite confident from some experience that I have had in the publishing line that the real difficulty is in securing a fair amount of advertising that would pay part of the cost of publication. I do not believe that the advertising space rate could be placed at a very high figure, or corresponding with that of a much more widely-circulated journal as, for instance, the journals of the American Chemical Society. No doubt there is a great amount of material that could be included without any embarrassment. There is advertising matter which could not be included at all, and for which the advertisers would be willing to pay much more. Probably the advertising that undesirable material would not be accepted would obviate any trouble between the management and the publisher.

I have had some question about the need for a journal and material other than purely official material, yet I am satisfied that the need exists in some degree and that it would be a drawing feature; there is already on the part of the management of the journals of the American Chemical Society the need for space. The result is constant pressure on the part of the editors to restrict the volume of publications. That, undoubtedly, is desirable in many instances, just because it is desirable to eliminate matter that is not of major importance, but it results also in the restriction or elimination of discussions, which many of the papers merit.

I feel, furthermore, that official publications, such as those we have in mind, ought to be strictly in the hands of the officials responsible therefor, and that we should be able, representing as we do, not simply individuals, but institutions, to provide means for the satisfactory publication of that material, which we have gotten together because of the mandates of the institutions which we represent. I have no doubt at all, speaking for my own institution, that we could increase in reasonable proportion, our institutional subscription for the support of the association. There

would be absolutely no objection to caring for part at least of the publication expenses until the journal could be gotten on its feet by advertising and subscriptions. There is no question in my mind that many might rely on the trade journals for their information without coming to us for it. There are ways by which copy of such material might be restricted. The question of wisdom and policy is another matter of great importance. Still speaking as one of the members and representing one institution, I will say that I am ready to do what I can to help get our publications out.

TROWBRIDGE: I have one or two points to bring out. This is an official body representing not individuals but institutions. There will be no difficulty in getting our institution to pay its part toward the publication. I suggest that each institution pay $25 or subscribe for five copies of the journal. Then, as individuals, all are willing to pay subscriptions for personal use for financial help. I feel that it would be an advantage to have our own journal rather than have our proceedings published in the journal of some other association.

HARTWELL: I am opposing the publication of a journal for the sake of discussion, not from personal opposition. All the States would not be ready to subscribe four or five copies and the individual analyst would be more handicapped than when volumes could be purchased by individuals. The matter might be presented to the Department of Agriculture that the proceedings be printed and sold but not given out. I, too, regret a little bit the multiplication of journals, and I have in mind the thought that possibly our prime work is in connection with analytical methods. Possibly this association can scarcely interest itself in the practical questions of agricultural chemistry. Possibly it has so much to do now that we can scarcely hear any number of agricultural papers unless they have to do with the analytical methods. A section of the American Chemical Society has already studied this question. It has been indicated by some that our Journal of Industrial and Engineering Chemistry is already overcrowded. If it were not, it seems to me it is not an inappropriate place to have a boiled down record of our proceedings. The methods could be taken care of in some way by the sale of an appropriate volume that could be secured by anyone at a nominal cost. I doubt a little if this association can broaden out to take up broad questions of agricultural chemistry, and I would like to leave these thoughts with those in authority while considerng this matter.

BRINTON: There has been much discussion about what the American Chemical Society can do. I think that while I have no authority to make this statement that there is no possibility of counting on the American Chemical Society to do anything, the consensus of opinion is that it is absolutely impossible to count on them. There would be no possibility of getting a fourth journal without increasing the dues of the American Chemical Society, so that we might as well abolish at once any hope in that direction.

It seems to me that there is no question but what we should devise some way of having our proceedings and methods published and it is only a question of the ways and means. Other organizations have published their proceedings, do it every year, and as Dr. Alsberg has explained, it is only a question of practically putting up a guaranty fund of $1,000. When he sent out the letter in June that we would have to guarantee $3,000, I thought it was practically impossible, but $1,000 does not look that way. Therefore, I believe that if the matter is taken up in the proper manner, this material can be published and in order to promote discussion, I make a motion that the association publish its proceedings and the methods of analysis,the method of financing to be decided later by the present committee or the committee to be appointed.

PRESIDENT: Moved and seconded that the association publish its proceedings, leaving as I understand the details to the executive committee. Any discussion of this question?

DAVIDSON: I would like to ask Dr. Alsberg if he has any estimate for publishing the proceedings as a separate volume? I want to say that I am rather opposed to the publication of a journal, whether we should call it an agricultural journal or a journal of this association, because I think we have altogether too many journals now and the financial side should be considered very seriously. I do not think we ought to burden the members with another journal, and that if we could in any way publish the proceedings of the association by themselves and then the methods of analysis as a separate volume that would be used as a kind of textbook for which a price could be charged, I believe that the demand for that book would be sufficient to pay the expenses of its publication and probably a great part of the expenses of the proceedings, and I think it would be advisable for the Executive Committee to take up that side of the question. It could be turned over to a a printer and he would be responsible for financing it until such time as the revenue amounted to enough to float it. I do not know whether you could get enough members to pledge to purchase them. It has been suggested that in the publication of a journal we would get considerable advertising matter, but I do think that the demand for the methods, which of course would not include advertising matter, would be sufficiently great to pay for the publication of both and for that reason I am rather opposed to that journal.

FRAPS: It appears to me that in order to get these proceedings, whether by journal or in a separate volume, it will be necessary to make some changes in the Constitution of this organization, especially in regard to the dues that are being paid. In order to raise a guaranty fund, or to provide for the publication of the proceedings, the present dues, will have to be increased. This is an official organization representing official bodies and it is quite possible that we should have two or three classes of dues. The experiment station offices, or such offices, could pay comparatively large fees, say $10 or $20. The Association of Agricultural Colleges and Experiment Stations, I think, charge as much as $35 a year for the organization. Next, it might be advisable to have contributing members composed of, I am a little doubtful about this, but composed of organizations not official—but who are vitally interested in these matters, who might pay $2 which would give them an opportunity to contribute to the publications of these meetings or to finance this journal. Then, in the third place, we could have individual members who might pay individual dues at a fee to cover the approximate cost. In that way, we would have official recognition of the various bodies that compose this organization, and the burden would be shifted from the individual members where it does not belong to the body where it does belong. I do not know what difficulty would be in the way of the different stations or departments in regard to the payment of these dues, but these large dues are paid by the Association of Agricultural Colleges and Experiment Stations and they publish their proceedings from these fees. This appears to me to be the chief thing to be settled, the financial end.

The manner of the publication is, of course, a separate and distinct matter for consideration. The dues, which I believe are $2 at present, are insufficient to raise any guaranty fund. This organization, with that amount of dues would not be in position to guarantee any amount of money and it does not appear to me to be compatible with the dignity of this organization to ask individuals to place financial obligations. It should lay upon the organization where the benefit is conferred.

I am rather in doubt as to whether to publish a journal or separate. Both have their advantages. The journal would get better postage rates, but, on the other

hand, the separate proceedings would be one publication and would be recognized as official.

VAN SLYKE: I have nothing in the way of suggestions to offer. My own attitude of mind is, the more suggestions that are coming in, the less I know where I am. I do feel this, that we are practically abandoned by everybody, and that we have been practically thrown into the stream and told to swim out if we can. I believe that we can. Even the publication of a quarterly journal, involving a guaranty fund of $1,000, seems not unreasonable. It seems to me that it ought to be within easy reach of attainment. After Dr. Alsberg's report this morning I felt more encouraged than I have at any time before. It seems to me that it would be a disgrace for the association to say we cannot do anything—we cannot publish our methods. Personally, I believe that there is room for a journal. I am rather glad that it is practically impossible for the American Chemical Society to take it up, because, so far as I have known, the attitude has not been altogether one of apparent satisfaction. It may be that the financial question is the whole thing back of it. I have been quite dissatisfied with the publication of any of our papers in the Journal of Industrial and Engineering Chemistry; it seems that the articles pertaining to agriculture are rather lost sight of in a journal of that sort.

I think that we ought to come to some decision here today, or at least to come to a decision that will be the basis of action. I would like to ask one question for information. Is the Department of Agriculture, is the Secretary of Agriculture, willing to publish the methods, or is it definitely decided that the Department will not publish our methods?

ALSBERG: It has not been definitely decided that the Department will not publish the methods. In fact, I have not taken that particular question up seriously. I have no reason to believe that Bulletin 107, Revised, cannot continue to be published by the Department. I can find out very easily in a few moments if that is desired, but I will say that the present administration of the Department feels that its printing funds are enormously overtaxed, that the Department's mission is very largely an educational mission, and as to the publication of a bulletin of official methods, while the Department probably would be willing to continue them, it would rather welcome the idea of being able to spend that sum of money on publications that will have the educational value that, of course, Bulletin 107, Revised, has not. It is a technical bulletin and the tendency of the Department is to promote the publication of technical matter in a technical journal, and confine its publications to the things that are of immediate educational value. That is at present the tendency of the Department.

I want to answer the question which Dr. Davidson asked me when I was called to the telephone. You asked me the cost of printing the Proceedings and Bulletin 107, Revised. I can tell you pretty definitely. The average cost to the Department is $1,700 for the proceedings and it costs in the neighborhood of $2,500 to publish Bulletin 107. That does not include, as I remember, the cost of stenographers, typewriting, and other clerical work, which is very heavy. I believe the cost of proof reading, typewriting and editing the proceedings took about one-third the time of the editor of the Bureau of Chemistry. The cost of editing Bulletin 107, Revised, is not so great as the cost of editing the proceedings, because the manuscript is in very much cleaner shape and is about ready to print. But still these figures do not include all this stenographic, editorial, and clerical work.

Now, of course, we know the cost to the Government to do printing is commonly believed to be greater than it is in ordinary commercial work. It does more careful work in some ways, uses better paper, and there are other reasons probably why

it costs a little more to print the thing through the Government than otherwise. Now the cost of printing the proceedings could be considerably reduced by cutting down discussions, printing on paper that is not quite so good, and economizing in that way.

I do not think the cost of printing the proceedings could be less than $1,200 unless we cut them down a great deal, and probably for not less than $1,500, and the official methods, which include a certain number of illustrations, would be several hundred dollars more than the proceedings. It will depend upon the degree to which we are willing to cut the thing down. I can get very accurate figures if that is desired.

LADD: Owing to the method in which the Government makes its publications would it not take much longer to get it out by the Government?

ALSBERG: Of course the commercial printer could turn it out as soon as he gets the manuscript and there could be a penalty if he did not turn it out in a reasonable time. My experience is in the Government that you can get an emergency printed overnight, but when it comes to a bulletin we would consider it quick work if we got it in six months and probably in eight or ten. I know of one case when a bulletin did not appear for two and one-half years after the manuscript was submitted. Dr. Bigelow has had more experience than I along this line. Isn't it your experience that six months and probably eight are required?

BIGELOW: The best is three after they have the manuscript, and then whether you get it in three months is whether Congress is in session and if Congress is in session it takes considerably longer.

ALSBERG: So the main trouble is you could not guarantee how long it would take. It might be two or three or four or five or six months and probably six or eight.

BIGELOW: And whether the funds give out.

MCDONNELL: One thing that occurs to me, and that is, the fact that we would probably want the proceedings all in one part, and that would make the most of the publication come in only one part, while the other three parts would be small, or if we had to publish the methods, provided they are not published by the Government, that would make another large volume, for which there would no doubt be a special demand, and there should be an extra edition but the other consideration as to how it is proposed to divide the four or more parts would be a problem.

ALSBERG: There are two chief advantages. One of them is that the printer is willing to give a better figure on work that comes regularly, so that he can provide regularly for it, and the other feature is, of course, the Post Office rates on mailing are favorable to a periodical. Those are the only advantages in having a periodical.

MCDONNELL: Was it proposed to divide the proceedings into four parts?

ALSBERG: Well, I think those are details which the committee did not consider. I had in mind that we wanted it a quarterly, but it did not need necessarily to be issued at intervals which were three months apart; that it would be issued as fast as the material could be gotten together and the proceedings put into the first number as far as they could be. If they could all be put into the first number, well and good, and if not all right, then into the next number, etc. That had really not been discussed.

MCDONNELL: It is necessary to state to the postmaster when the publication will come out.

ALSBERG: I had not looked up that special feature. I did not know that it was necessary to state that it would appear at stated intervals.

MCDONNELL: I published one and I know it is necessary to state when it will appear in order to get the cheaper rates. They rather prefer that you state it will

come out at a certain time, but if it gets out any time within the quarter the Post Office authorities make no objection. As soon as it gets out of the quarter they do object.

DAVIDSON: I would move that this matter be referred today to the committee and that they make provision for the publication of the proceedings and the methods not as a journal, but as those two publications. I believe that is better than to refer it to the committee and have them wrangle over it.

BRINTON: I think that was my original motion.

LADD: An amendment has been accepted that the Executive Committee be authorized to publish the proceedings and methods of analysis, leaving it for them to decide as to how they are to be published.

VAN SLYKE: Are they authorized to raise the fund?

LADD: I am inclined to think you would have considerable trouble.

DAVIDSON: Would this publishing house be willing to take it.

ALSBERG: They would not take over any of the risk. Under this arrangement they probably take over two-thirds of the risk, and they make a fairly reasonable price, I think, calculating that price on a basis of 10 per cent over what it costs them. No doubt we could get it done a great deal cheaper by an ordinary printer, and that would be the most advisable thing if we are going to print just the proceedings and the transactions. We might just as well have it done as a job of printing. We could probably make a contract with this concern to do it somewhere in the neighborhood of $1,500.

TROWBRIDGE: I do not feel that we ought to turn down the proposition of the journal after the report of the committee, which has made the investigation it has and has made the recommendation it has. I think we can see at a glance that this publication of the journal could include without any difficulty the publication of methods because we would get our revisions more rapidly in that way. We would get it in parts with separate pagination so that as soon as the revision was complete we would have no difficulty in binding it in the one volume of the revision, and furthermore, the committee could continue with separate pagination for methods as fast as they were completed, so that we could always have our methods up to date to incorporate as an addenda. I would like to see either the Executive Committee or a special committee have the right to make the arrangement as to which ever way they see fit, and I would like to offer an amendment to give the committee power to make it a journal if, in their opinion, it seems best.

Seconded.

LADD: Instead of putting up a guaranty of $1,000 I feel confident that if we are to publish the proceedings and Bulletin 107, Revised, we will have to guarantee to some publishing house between $3,000 and $4,000 and pay for it as soon as it is published. I just mention that as one of the incidentals in the work of the committee in the past year.

DAVIDSON: Won't it be pretty hard to get $1,000? Of course it would be much easier to get $1,000 than $3,000 or $4,000. Suppose that we could finance it in any way, I believe that we could sell 1,000 copies at $2 each. Of course I recognize the fact that the financing is awfully hard. How are we going to finance it at all is the important question before the association as a whole.

LADD: I think Dr. Alsberg's statement was that $205 had already been pledged. I know that I have promised to guarantee a certain amount and others have done the same. You left it in the hands of the committee last year. The committee have not felt that they were in position to go ahead because they did not have a financial backing, and I do not want to see it left so that it will prevent the publication for another year.

DOOLITTLE: There is one question that has bothered me a little bit, not knowing whether or not it would make any difference to the experiment stations whether this was published in the form of a journal or in the form of proceedings. I feel that as Dr. Fraps has said that the expense ought to go back to the institutions whom we represent, and the question has arisen in my mind whether or not it will make any difference with these officials whether or not they were paying for a volume of the proceedings or whether they were paying for a journal.

FRAPS: I will say that as far as our institution is concerned I think we can pay dues of $10 or $25, but I do not think we could subscribe to five volumes of the journal.

PRESIDENT: The details can be worked out later. Let us come back to the motion authorizing the Executive Committee to publish the proceedings of this association, either as a single volume of proceedings or as a quarterly, if I understand it correctly, including the methods. All in favor of question say yea, opposed nay.

Motion unanimously carried.

FRAPS: I move that a committee of three be appointed to consider the question of dues so as to assist this committee.

MCDONNELL: We now have two years' proceedings due, how about last year's proceedings? We should have enough material to proceed at once and get out 600 pages.

ALSBERG: The 600 pages was just a provisional basis for the publishers, and they took it on the basis of other scientific journals. We could get the same contract in proportion for any number of pages we want, if we publish one volume in one year or two years as we wish.

ABBOTT: The status is that the Executive Committee are to have that published and they have to wrestle for the wherewithal to get that done. Well, we have them in a pretty good hole. We might leave them here and let them get out as best they can, but it strikes me it might be a good plan to devise a scheme to assist them out of that predicament. How are we going to get that money? Personally, I would be one of ten or twenty or fifty to guarantee $10 or $20 or $50, if necessary, to this Executive Committee to pay for the printing of that material. I do not know how the association feels about that, but I do not know how else we are going to get it except by every fellow who is interested to make such a personal guaranty.

FRAPS: If the dues are made sufficient, the association will be in position itself to guarantee that.

LADD: Is the motion by Dr. Fraps seconded?

TROWBRIDGE: I would like to offer a motion that this come from the Executive Committee, and that they prepare a circular letter to all our departmental and station libraries, asking them to find out, or asking them directly to guarantee a fee of $25 to cover that.

DAVIDSON: Dr. Fraps says that would be against the Constitution. Now we would like to see a copy of the Constitution.

ALSBERG: (Answering a previous question) 2746 copies of Bulletin 107, Revised, were sold by the Superintendent of Documents and about 400 copies given out by the Bureau of Chemistry during the year July 1, 1913 to June 30, 1914.

LADD: The By-Laws state that the annual dues shall be $2. Of course then it will be necessary to change the By-Laws.

MCDONNELL: It seems to me that so far as the guaranty is concerned that the members will have to guarantee that. I hardly think that our institutions would take up a guaranty of $50 or $100. It seems to me that that will have to be done personally. It seems to me that we ought to be able to guarantee at least $1,000.

DAVIDSON: I think the Executive Committee in looking over the number of institutions that are represented here can figure out the probable cost and then simply

write the circular letter saying how much the dues shall be. It could be taken up with the heads of the departments and they could be asked if they are willing to pay $10 for the benefit of the institution. So I move that the By-Laws be changed in regard to the question of annual dues and that the amount to be levied shall be left to the Executive Committee.

PRESIDENT: Dr. Trowbridge withdraws last motion.

Motion of Davidson carried.

REPORT ON DAIRY PRODUCTS (ADULTERATION).

By JULIUS HORTVET (State Dairy and Food Department, St. Paul, Minn.), *Associate Referee.*

Following the recommendations adopted at the meeting of this association last November, the work of the present year has been directed toward a further study of the modifications of the continuous extraction method for determining fat in evaporated milk, sweetened condensed milk, and cream. The work has included also comparative fat determinations by means of the Roese-Gottlieb method. Owing to the difficulty of arranging for the preparation of suitable samples of ice cream to be forwarded to the collaborators, it has been deemed advisable to carry out the modifications suggested at the last meeting on samples of ordinary sweet cream. In accordance with the plan of the work decided upon, arrangements were made with the factory of Borden's Condensed Milk Company, at Norwich, N. Y., for the preparation of the samples. Particular care was taken to insure the preparation of uniform samples and that the samples were to be representative of products manufactured under commercial conditions. They included: (1) Sweetened condensed milk; (2) unsweetened evaporated milk; (3) canned sweet cream.

The plan of preparation of the samples for the fat determinations is similar to the procedure carried out in the work of 1913 and differs in no essential respects from the usual procedure. The aim has been to adapt the method of preparation to the character of the sample to be extracted. The description of the methods as submitted to the collaborators is given as follows:

METHODS SENT TO COLLABORATORS.

A. DETERMINATION OF FAT BY THE METHOD OF CONTINUOUS EXTRACTION.

(1) *Preparation of sample.*—If the milk be sour, obtain an even emulsion by repeatedly pouring the sample back and forth from one container to another, with slight warming if necessary. Unless a fine, even emulsion can thus be secured, it will not be expected that a satisfactory determination can be made. In the case of evaporated milk or thick cream, mix the sample thoroughly, best by transferring the entire contents of the can or bottle to a large evaporating dish and working with a pestle until homogeneous throughout. In preparing ice cream, soften the sample by careful warming to the consistency of ordinary cream, transfer to a beaker and stir until homogeneous throughout.

(2) *Method for milk, evaporated milk, sweetened condensed milk, thin cream, and ice cream.*—Into a 1,000 cc. beaker weigh 100 grams (in the case of milk 200 grams) of sample. Add 300 cc. of water, mix thoroughly, and heat to boiling. Add while boiling, very gradually, 25 cc. of Soxhlet's copper sulphate solution, diluted with 100 cc. of water. In a Büchner funnel wet a filter of suitable size and of loose texture, filter with suction and wash three times with a little boiling water, filtering as dry as possible. Remove the cake, which should be dry enough to be broken up easily between the fingers, break into small particles, and dry in the open air overnight. Grind in a mortar with sufficient (usually 25 grams) anhydrous copper sulphate, let stand a few minutes, or until the product seems quite dry and not at all lumpy. Into the inner tube of a large Soxhlet or other extraction tube place a layer of anhydrous copper sulphate, then the powdered mixture. Place on top a loose plug of cotton and extract 16 hours with pure ethyl ether. The ether should be poured into the extractor and allowed to percolate through before the heating is commenced. About 50 cc. of the solvent will be required. Evaporate the ether slowly on a steam bath, then dry the fat in an oven at 100°C. until loss of weight ceases. Reserve the weighed fat for further examination if required.

(3) *Method for rich cream and thick ice cream.*—In a Büchner funnel wet an 11 cm. filter of loose texture and cover with a thin layer of fibrous asbestos mixture, being careful to cover the sides as far up as possible. In a 250 cc. beaker boil 25 cc. of Soxhlet's copper sulphate solution, and add, while stirring vigorously, 50 grams of the material. Immediately remove the source of heat and filter with slow suction. Wash once or twice with a small amount of cold water, and proceed as in the method described under (2).

B. DETERMINATION OF FAT BY THE ROESE-GOTTLIEB METHOD.

Weigh 40 grams of the properly-prepared sample, preferably in a tared weighing dish used for sugar analysis, transfer by washing to a 100 cc. graduated sugar flask and make up to the mark with water. Measure 10 cc. of this solution into a Röhrig tube (Zts. nahr. Genussm., 1905, **9**: 531) or into a suitable size Werner-Schmidt extraction apparatus, using for the purpose not more than 10 cc. of water. To the material in the extraction tube add 1.25 cc. of concentrated ammonium hydroxid (2 cc. if the sample be sour) and mix thoroughly. Add 10 cc. of 95 per cent alcohol and mix well. Then add 25 cc. of washed ethyl ether, shake vigorously for half a minute, add 25 cc. of petroleum ether (redistilled slowly at a temperature below 60°C. preferably) and shake again for half a minute. Let stand 20 minutes or until the upper liquid is practically clear and its lower level constant. Draw off the ether-fat solution as much as possible (usually 0.5 to 0.9 cc. will be left) into a weighed flask through a small quick-acting filter. Re-extract the liquid remaining in the tube, this time with only 15 cc. of each ether, shaking vigorously half a minute and allow to settle. Draw off the clear solution through the small filter into the same flask as before and wash the tip of the outlet, the funnel, and the filter with a few cubic centimeters of a mixture of the two ethers in equal parts. Extract again and wash in the manner just described. Evaporate the ether slowly on a steam bath, then dry the fat in a water-oven until loss of weight ceases.

RESULTS OF COÖPERATIVE WORK.

The results submitted by the collaborators are shown in the following tabulation.

Nearly all collaborators report difficulty in obtaining satisfactory results on the sample of cream owing to the more or less separated or churned

Analysis of dairy products.

ANALYST	SWEETENED CONDENSED MILK		EVAPORATED MILK UNSWEETENED		CREAM	
	Continuous extraction method	Roese-Gottlieb method	Continuous extraction method	Roese-Gottlieb method	Continuous extraction method	Roese-Gottlieb method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Miss N. A. Childs, Lansing, Mich.	9.98	10.11 9.86	7.24 6.79	6.78 6.76	....	26.17 27.24
F. L. Shannon, Lansing, Mich.	9.19 8.71	8.65	7.53 7.17	7.27 7.55	....	31.49 ....
A. S. Wells, Portland, Ore.	9.04	9.03 9.08	7.61 7.55 7.04	7.74 7.80 7.68 7.75 7.59	28.14	28.56 26.15 30.27 30.69
G. B. Taylor, New Orleans, La.	8.62 8.65	9.12 9.09	7.28 7.28	7.74 7.66	....	....
C. L. Clay, New Orleans, La.	....	....	....	....	28.96 28.68	28.62 28.08
C. L. Black, Philadelphia, Pa.	8.88 8.79	9.02 9.01	7.22 7.27	7.51 7.49	....	....
C. C. Forward, Ottawa, Can.	9.03	9.54 9.50 9.45	7.04 6.92	7.99 7.98 7.99	....	29.57 28.81 29.13
C. B. Gnadinger, Chicago, Ill.	8.83 8.75	9.08 9.07	7.64 7.55	7.78 7.77	27.65 27.46	28.00 27.96
G. G. Parkin, St. Paul, Minn.	9.10	9.50	7.48	7.82	29.24	29.10
R. S. Hollingshead, Washington, D. C.	....	8.77 8.94	....	7.37 7.50	....	28.78 27.52
L. B. Burnett, Washington, D. C.	8.57 8.54	8.65 8.72 8.43 8.38	6.91 7.00	7.30 7.42 7.35 7.58	26.00 28.00	27.65 27.16 26.18 26.27
J. O. Clarke, Atlanta, Ga.	8.62 8.71	8.65 8.58	7.28 7.23	7.40 7.37	26.55 26.43	26.63 26.60
L. W. Ferris, Washington, D. C.	8.81	9.19 9.17	7.27	7.72 7.75	....	....
J. T. Keister, Washington, D. C.	9.00	9.11 9.10	7.33	7.74 7.75	.....	....

condition when the sample was received. With only two exceptions, the other samples appear to have been received in good condition. Unfortunately, the manufacturer appears to have misunderstood or overlooked the directions for the preparation of the canned cream. The plan of the work required that the cream contain a comparatively low percentage of butter fat, 15 to 18 per cent. On examining these samples, however, it has been somewhat disappointing to discover that the butter fat test gave high results, and many collaborators have encountered almost insuperable difficulties in carrying out the directions for the continuous extraction method. These results are nevertheless included in the tabulation, but are not to be considered in any way as contributing for or against the adoption of the proposed modified continuous extrac-

tion method. The chief interest centers on the results reported on the samples of condensed and evaporated milk. It should be stated at the outset that the showing is in general rather disappointing. The results have been obtained by a comparatively large number of collaborators, all of whom have doubtless had considerable experience and represent leading laboratories in various parts of the country.

The following comments and criticisms were made by the collaborators:

COMMENTS BY ANALYSTS.

C. C. Forward: The rich cream was churned and butter fat separated so that sampling was very difficult for the Roese-Gottlieb method, which would account for differences. Continuous extraction method was not satisfactory, as fat was separated and would not form into a cake on precipitation. I would suggest that this difficulty might be overcome by mixing the cream with skim milk so that the proportion of casein to fat would be increased sufficiently to give a precipitate which would filter dry enough to form a cake. This has not been tried as time is not available. The Roese-Gottlieb method gives results somewhat higher than the other method and higher than asbestos extraction method (Babcock asbestos method) but the fat obtained seems quite pure.

In addition to results obtained on samples submitted, a statement is made of tests on samples obtained locally. These samples included a condensed milk, "Diploma" brand, manufactured in England, and a cream, Ottawa Dairy, 28 per cent. The results were as follows:

	Condensed milk fat per cent	*Ottawa cream fat per cent*
Roese-Gottlieb method	10.47	29.20
	10.43	29.05
	10.55	29.13
Continuous extraction method	10.08	.....
	10.00	.....

Miss N. A. Childs: I found by adding the first 50 cc. of the copper sulphate, drop by drop from a pipette, that a precipitate was formed which gave little or no trouble in filtering. The original method is very unsatisfactory for cream. The modification is fairly satisfactory, although I was unable to obtain a curd that would dry. In condensed milk more or less organic matter, probably sugar, is abstracted by the ether. Results are undoubtedly high.

L. B. Burnett: The discrepancies in the results on Sample 3 (cream) were due to the inability to secure uniform sample. It was thought that the low result, 26 per cent, Paul method, Sample 3, was caused by the fat having a tendency to filter through. This filtrate was extracted with ether, a correction of only 0.015 per cent being necessary. I think the Paul method for rich cream and samples containing a high amount of fat will work satisfactorily.

H. S. Bailey: The condition of No. 3 (cream) by the time we were ready to work on it was such that it was practically impossible to obtain a satisfactory sample. To this fact I attribute the great discrepancy between the different determinations. I am at somewhat of a loss, however, to understand exactly how Mr. Burnett obtained 26 per cent of fat by the Paul method in one of his determinations and I would have had the work repeated if the sample had not spoiled in the meantime. The butter fat has a tendency to run through the asbestos pad with rich creams, but apparently the low figure is not due to this difficulty.

A. S. Wells: The sample of sweet cream had churned and was in such a bad shape that I found it practically impossible to get an emulsion as desired. I find that it is a good plan in preparing the filter in the Büchner funnel to use two sheets of the filter paper. They readily separate after filtering and make the work more satisfactory. My principal difficulty in this method I found was to get the extraction apparatus to siphon over. After several experiments, however, this difficulty was overcome.

George B. Taylor: In the continuous extraction method very good separations were obtained and the material filtered readily. For the condensed and evaporated milks a Büchner funnel with a linen filter covered with an S. & S. No. 597 filter was used. Continuous extraction was carried on for 22 hours. Although I obtained good duplicates in every case, I am at a loss to understand why in my work the continuous extraction did not check with the Roese-Gottlieb method. While my assistant (C. L. Clay) did not get good duplicates, the two methods check more closely with him than they do with me.

L. W. Ferris: In the Paul method the extraction was difficult because the mass packed and prevented the siphoning of the ether. The method is a good way of getting pure fat for further examination but apparently gives results lower than the Roese-Gottlieb method.

J. T. Keister: The Paul method was unsatisfactory, the difficulty being the packing of the sample in the extraction tube thus preventing the proper siphoning of the solvent. This difficulty seemed greater in the case of evaporated milk. A much smaller charge (20 or 25 grams) seems advisable, also the use of some material—as pure washed sand—mixed with sample to prevent packing.

The above comments add further discouragement respecting the reliability of the continuous extraction method when applied to condensed and evaporated milk. Also, the fact should be clearly emphasized that the results obtained by the Roese-Gottlieb method, while in the main higher and somewhat more uniform, are far from being satisfactory.

Fat determinations (1913).

COLLABORATOR	SWEET CREAM		HOMOGENIZED CREAM		CREAM WITH OLEO OIL		ICE CREAM	
	Roese-Gottlieb method	Continuous extraction method	Roese-Gottlieb method	Continuous extraction method	Roese-Gottlieb method	Continuous extraction method	Roese-Gottlieb method	Continuous extraction method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. H. Biesterfeld	....	....	15.51 15.55	15.49 15.53	....	....	17.34 17.35	.... 17.33
C. B. Gnadinger	13.96 14.06	13.68	15.51 15.51	15.53 15.56	21.75 21.89	23.12	17.34 17.19	17.29 17.26
L. B. Burnett	13.27 13.32	15.34	14.45 14.60	15.58 15.52	20.3 20.0	22.29 22.18	16.52 16.66	17.28 17.26
C. C. Forward	15.03 14.95 15.11	15.04 14.48	15.39 15.00 15.29	15.46 15.48	....	22.70 22.73	17.55 17.42 17.18	15.63 16.97
G. G. Parkin	11.02	14.42 14.31	15.49	15.34	21.82	22.34 22.27	17.37 17.40	17.23 17.30

It should be recalled in this connection that the results reported by a smaller number of collaborators in 1913, on sweet cream, homogenized cream and ice cream were in general quite favorable; and for purpose of comparison at the present time these results are herewith included.

Many of the collaborators who have submitted reports during the present year have had experience with similar work in years past and some are included among the collaborators of 1913. As already stated, all or nearly all collaborators are experienced analysts and represent eight well-known laboratories. A critical examination of the tabulated results tends to the conclusion that there are peculiar difficulties attending the determination of fat in evaporated and condensed milk—difficulties which possibly have not heretofore been fully realized. The collaborators, doubtless, in some instances reported results which should have been omitted, that is, some results may have been reported which were recognized as faulty and represent first-trial attempts. These, however, are included in the tabulation, as no definite information has been obtained concerning the relative merits of the different results submitted. In the main the results obtained by the continuous extraction method, both on the samples of sweetened condensed and unsweetened evaporated milk, are decidedly lower by the continuous extraction method than by the Roese-Gottlieb method.

An inspection of the results cannot fail to reveal the probable composition of the samples prepared by the manufacturer. It is a very safe prediction that the samples of unsweetened evaporated milk were made to contain not less than 7.8 per cent of butter fat. Nevertheless, there are twelve results obtained by the Roese-Gottlieb method which are so seriously low as to attract attention. A similar state of affairs is revealed among the results obtained on the samples of sweetened condensed milk. There are evidences that each collaborator has, however, succeeded in obtaining fair check results in his own laboratory. The great discrepancies appear to occur among the results obtained by different individuals. Personally, the associate referee has full confidence in the Roese-Gottlieb method as a reliable procedure for the determination of fat in evaporated milk, and the same opinion will doubtless be expressed by every analyst who has had considerable experience in the analysis of products of this kind. It is unlikely that the various collaborators deviated materially from the procedure as outlined in the directions given, yet, just where the difficulty lies it is impossible to point out. The conclusion seems inevitable that there is here indicated an imperative demand for a special investigation into the details of the various methods for determining fat percentages in condensed and evaporated milk. It is quite likely that the difficulties are not serious, but it is at the same time plain that they exist, and that there is somewhere a lack of adequate understanding among

analysts respecting essential features which may be peculiar to such products as have been considered during the past season.

Two collaborators who reported that the samples of evaporated milk had changed somewhat in shipment, stated also that no great difficulty was experienced in preparing the samples in proper condition for analysis. It is too early to conclude that the continuous extraction method is incapable of yielding at least fairly accurate results; on the other hand, it appears to be well worth while that a further attempt be made to correct deficiencies and to modify the method with a view of clearing up a number of obscure points. Also, in view of the general application of the Roese-Gottlieb method, it appears to be seriously demanded that this association recommend that special attention be given to this method, with a view to correcting deficiencies if any such actually exist. While the results obtained in 1913 were far more favorable, although reported by a smaller number of collaborators, no recommendation can be made in favor of the final adoption of the continuous extraction method at this meeting. The situation which now seems most worthy of consideration is the status of the Roese-Gottlieb method applied to evaporated and condensed milk, and it is therefore urgently brought to the attention of this association that some action be taken with a view of the study of this or any one or two other methods that may be proposed. Whether it is possible to expect much more uniform results than are shown herewith among collaborators working in different parts of the country under different conditions and possibly on samples arriving over long distances, it is not easy to predict. There is also always the chance that samples are not strictly uniform in composition. Nevertheless to any one who has had daily experience in the analysis of these products during the past few years, taken in connection with the general showing presented in this report, it must seem imperative that this association give some serious attention during the coming year to a study of methods for the determination of fat in sweetened condensed milk and unsweetened evaporated milk.

C. W. Bradbury of the Chemical Laboratory of the Virginia Department of Agriculture at Richmond, read a paper on "The Alkali Method for the Determination of Fat in Ice Cream and Condensed Milk," the essential facts of which had been published as Circular No. 42, of the Dairy and Food Division of Virginia.

No report was made by the associate referee on cereal products.

REPORT ON VEGETABLES.

By E. W. Magruder (Department of Agriculture, Richmond, Va.), *Associate Referee.*

CANNED FOODS.

Last year the work on vegetables consisted in determining the per cent of easily-separable fluid found in canned tomatoes. In that report the results of the examination of 77 cans of tomatoes were given and the average amount of easily-separable fluid was found to be 52 per cent with an extreme variation of from 38 per cent to 64.4 per cent and with 60 per cent of the samples ranging between 47 per cent and 57 per cent of fluid. It was recommended that the work be continued and that other canned foods be included in the study.

The work recorded in this report has been done by J. B. Robb and the associate referee and has consisted in the examination of canned tomatoes, peas, and lima beans. Not only has the amount of easily-separable fluid been determined, but quite a detailed study of the fluid has been made, consisting in the determination of the specific gravity, the solids in the unfiltered and filtered liquid, the immersion refraction index, and in some cases the polarization. An endeavor was made to determine whether there was any constant relation or factor existing between the solids in the filtered liquid and the refractometer reading.

METHODS.

Separable fluid.—The method used was practically the same as that employed last year: Determine the weight of the contents of the can and transfer the material to a regular fertilizer sieve with round holes 1 mm. in diameter and stir the material gently with a spatula to allow the liquid to drain out, allowing the material to stay on the sieve 5 minutes in the case of tomatoes, and 3 minutes in the case of lima beans and peas, stirring gently just before the expiration of the time limit. Some liquid still remains with the canned material at the end of the time specified, but the great bulk of the fluid had drained away and the time specified is considered about right to allow the easily-separable fluid to drain off. This fluid is then weighed and the per cent of easily-separable fluid calculated. Measuring the contents of the cans and the fluid was tried and the results were about the same as obtained by weighing, but on the whole weighing was found to be the easiest and quickest.

Solids.—Dry 25 cc. of this fluid on a steam bath and then in an electric oven for 3 hours at a temperature of 105° C., and calculate the per cent of solids. Filter a portion of this fluid and dry 25 cc. of the filtrate exactly as in the case of the unfiltered fluid and calculate the per cent of solids.

Refraction and polarization readings.—Use a portion of the filtered liquid at a temperature of 20° C. for the determination of both the refraction and polarization readings. The immersion refractometer and Schmidt and Hentch polariscope and a 100 min. tube were used. In many cases the liquid was so opaque that the polarization could not be read, so that few results are given.

Factor.—It was hoped that a factor of value might be obtained and in order to obtain one the refractometer reading was divided by the per cent of the solids in the filtered liquid. The results are given in the tables.

Five brands of canned tomatoes and two each of peas and lima beans were selected and a case of each was obtained. Three cans of each brand were examined in December, 1913; then three cans of each were packed in a case and shipped by express to W. F. Hand in Mississippi, who immediately shipped them back, thus giving them a journey of about 2,000 miles. After their travel they were examined in January, 1914. This was done in order to determine what effect a long journey on the train with the jolting incident thereto would have on the contents of the cans. Three cases of each brand were kept without being moved and examined in July, 1914, which was seven months after the first examination and about one year after they had been packed. This was done to determine what effect age had upon the contents of the cans. Some other cans of beans and tomatoes were examined in the fall of 1913, and the results are given in the tables. There were also examined in October, 1914, samples of tomatoes of the pack of 1914 of two of the brands which had been examined previously.

RESULTS ON TOMATOES

Easily-separable fluid.—62 cans of tomatoes were examined and the average amount of easily-separable fluid found to be 50.7 per cent with a minimum of 31 per cent and a maximum of 66 per cent, or a difference of 35 per cent, which is greater than the lowest per cent. A striking fact shown is the very wide variation between cans of the same brand examined at the same time. This is shown in the case of the Cherokee brand, which varied from 31 per cent to 53 per cent with a difference of 23 per cent, and again varied from 39 per cent to 60 per cent with a difference of 21 per cent. Only about 100 cans of this brand were put up by a farmer for his own use and not for sale. They were usually put up in batches of about a dozen at a time, which may account for the wide variation. No water was introduced into the cans. In comparing the first results obtained with those after shipping and after standing it will be seen that shipping had practically no effect on the amount of fluid, but that age seems to increase the amount of fluid slightly. Some of the cans from the same cases are still on hand and we expect to examine them during next winter to see what effect six months more of age will have.

Specific gravity.—The specific gravity does not seem to bear any relation at all to the per cent of fluid, as some samples with a high per cent of fluid have a high specific gravity, while others with just as high per cent of fluid have a low specific gravity and vice versa.

Solids.—The solids in the unfiltered and the filtered liquid bear a close relation to each other. As a rule the unfiltered fluid has the most solids,

TABLE 1.

Canned tomatoes.

No. of sample	Brand	Location	Examined December, 1913							Shipped by express 2,000 miles and examined January, 1914							Kept in one place and examined July, 1914						
			Liquid	Specific gravity of liquid	Solids in liquid	Solids in filtered liquid	Immersion refractive index of filtered liquid at 20°	Polariscope reading (100 mm. tube)	Factor: Refractive index divided by filtered solids	Liquid	Specific gravity of liquid	Solids in liquid	Solids in filtered liquid	Immersion refractive index of filtered liquid at 20°	Polariscope reading (100 mm. tube)	Factor: Refractive index divided by filtered solids	Liquid	Specific gravity of liquid	Solids in unfiltered liquid	Solids in filtered liquid	Immersion refractive index of filtered liquid at 20°	Polariscope reading (100 mm. tube)	Factor: Refractive index divided by filtered solids
			per cent		per cent	per cent				per cent		per cent	per cent				per cent		per cent	per cent			
6166	F. F. V.	Fredericksburg, Va.	50.00	1027	5.33	5.07	39.1	..	7.71	57.0	1026	5.18	4.96	37.4	2.2	7.54	62.40	1022	4.90	4.80	[1]135.0	.....	.....
6166	F. F. V.	Fredericksburg, Va.	50.00	1026	5.19	5.05	39.4		7.80	58.3	1022	4.81	4.62	35.3	−2.1	7.64	58.34	1023	5.28	5.21	[1]133.5	.	.....
6166	F. F. V.	Fredericksburg, Va.	52.2	1026	5.02	4.90	38.4		7.85	53.0	1023	5.43	5.26	37.8	−2.4	7.18	60.38	1024	5.15	5.00	[1]132.5	..	.....
6167	New Kent	Toano, Va.	38.00	1026	5.35	5.28	39.9	...	7.56	41.5	1027	5.39	5.19	39.6	−2.5	7.63	43.73	1024	5.39	4.12	[1]131.6		.....
6167	New Kent	Toano, Va.	48.00	1023	4.89	4.86	37.3		7.66	48.1	1027	5.19	6.12	38.9	−2.2	7.60	42.08	1025	5.62	5.67	[1]138.0	−2.7	.....
6167	New Kent	Toano, Va.	40.7	1026	5.39	5.44	39.9		7.33	46.8	1027	5.43	5.30	40.4		7.62	52.44	1019	4.28	4.33	[1]131.0	...	.....
6168	G. B. Brand	Wilkersons, Va.	46.0	1021	4.03	3.86	33.2		8.60	51.90	1025	4.52	4.20	34.9	−2.5	8.31	52.72	1020	4.34	4.33	[1]127.5	...	.....
6168	G. B. Brand	Wilkersons, Va.	42.5	1022	4.21	4.06	33.9		8.35	53.80	1022	4.67	4.57	35.0	2.0	7.66	56.83	1020	4.33	4.39	[1]129.1	...	.....
6168	G. B. Brand	Wilkersons, Va.	48.7	1021	4.15	4.04	33.2		8.22	54.50	1021	4.38	4.13	33.0	−2.0	8.00	53.93	1020	4.16	4.29	[1]127.0	...	.....
6196	Maryland Chief	Baltimore, Md.	55.5	1025	4.84	4.69	36.5	.	7.78	52.0	1021	4.49	4.38	33.9	2.1	7.74	69.60	1022	4.49	4.67	[1]30.5	...	.....
6196	Maryland Chief	Baltimore, Md.	53.2	1023	4.60	4.42	34.8	..	7.87	66.7	1021	4.31	4.19	33.0	1.5	7.87	59.21	1020	4.19	4.50	[1]131.0	.....	.....
6196	Maryland Chief	Baltimore, Md.	47.0	1022	4.23	4.09	33.1	.	8.09	59.8	1022	5.06	4.92	35.5	−1.7	7.22	66.04	1021	4.49	4.73	[1]131.0	...	.....
6213	Cherokee	Chesterfield County, Va.	60.00	1029	5.53	5.34	40.2	−1.8	7.53	53.8	1026	5.37	5.06	38.8	−2.1	7.67	44.95	1026	5.67	5.42	39.2	−2.1	7.23
6213	Cherokee	Chesterfield County, Va.	49.3	1028	5.63	5.59	40.6	−2.3	7.00	33.7	1020	4.30	4.19	33.9	−1.9	8.09	46.80	1026	5.67	5.81	39.0	−2.0	6.71
6213	Cherokee	Chesterfield County, Va.	39.4	1026	5.20	5.21	38.3	−1.9	7.35	31.4	1021	4.55	4.51	35.3	−1.7	7.83	38.60	1023	5.02	5.17	36.5	−2.0	7.06
		Average	49.3	1024	4.90	4.80	37.2	..	7.79	50.8	1023	4.87	4.71	36.2	.....	7.71	53.8	1023	4.86	4.83	38.2	.....	7.00
6164	Jamestown	Richmond, Va.	37.7	1021	4.27	3.90	33.4	−1.5	8.59														
6164	Jamestown	Richmond, Va.	43.1	1021	4.17	3.90	32.6	−1.5	8.33														
6212	Hill Top	Chesterfield County, Va.	49.9	1019	3.76	3.74	32.1	−1.7	8.58														
6212	Hill Top	Chesterfield County, Va.	42.7	1018	3.49	3.42	31.0	−1.5	9.06														
6212	Hill Top	Chesterfield County, Va.	37.1	1018	3.42	3.37	30.3	−1.5	8.99														
6169	Monogram	Roanoke County, Va.	40.4	1025	4.98	4.97	36.8	....	7.42														
6169	Monogram	Roanoke County, Va.	56.9	1019	3.97	3.96	32.1	..	8.11														
6169	Monogram	Roanoke County, Va.	53.4	1026	5.34	5.39	38.8	.	7.19														
6170	Monogram	Roanoke County, Va.	58.6	1020	3.91	4.01	31.8	.	7.93														
6170	Monogram	Roanoke County, Va.	60.5	1020	4.15	4.15	32.3	......	7.78														
6170	Monogram	Roanoke County, Va.	54.2	1020	3.95	4.02	31.3	......	7.78														
		Average of all December results	48.3	1023	4.58	4.49	35.4	......	7.94														

[1] Liquid fermented before determination made, so results not used in the average.

Pack of 1914. Examined in October, 1914.

No. of sample	Brand	Location	Liquid	Specific gravity of liquid	Solids in unfiltered liquid	Solids in filtered liquid	Immersion refractive index of filtered liquid at 20°	Polariscope reading 100 mm. tube	Factor: Refractive index divided by filtered solids
			per cent		per cent	per cent			
6213	Cherokee	Chesterfield County, Va.	57.0	1026	5.02	5.27	39.6	−2.2	7.52
6213	Cherokee	Chesterfield County, Va.	63.3	1027	5.15	5.20	40.3	−2.3	7.75
6213	Cherokee	Chesterfield County, Va.	59.2	1026	5.22	5.25	39.9	−2.0	7.58
6212	Hill Top	Chesterfield County, Va.	44.2	1025	5.02	5.14	39.3	−1.9	7.65
6212	Hill Top	Chesterfield County, Va.	51.8	1024	4.93	4.90	38.3	−1.5	7.81
6212	Hill Top	Chesterfield County, Va.	45.5	1025	4.87	5.33	38.3	−1.4	7.19
		Average of all results	50.7	1023	4.76	4.69	36.2	....	7.77

but in quite a number of cases the reverse is true. This may be caused in part by the evaporation of some of the water during filtration, as the liquid filtered very slowly, but to reduce evaporation to a minimum the filtrate was caught in narrow-neck bottles. It is rather surprising to find that the filtered liquid contains about the same amount of solids as the unfiltered, the average amount of solids for all of the tomato samples being 4.76 per cent for the unfiltered fluid and 4.69 per cent for the filtered liquid.

Refractometer reading.—The results of the refractometer reading are quite interesting. They vary on the whole about as the percentage of solids, but here as in all the other determinations we have erratic results. The readings marked with a superior "1" were made on liquid which had fermented to some extent before they finished filtering, hence are lower than they should be, and are left out of the general average. On the whole the refractometer reading is more characteristic than any of the determinations, and as it is one of the easiest made it is probable that it furnished a better indication of the character of the liquid than any of the determinations.

Factor.—The factor obtained by dividing the refraction reading by the solids from the filtered liquid is not at all a constant one, although the variations are not as great as most of the other results obtained. It is doubtful if it furnishes any information of value.

Shipping does not seem to have any appreciable effect on tomatoes; age has a slight effect on the percentage of fluid, but apparently none on the composition of the liquid.

RESULTS ON CANNED GREEN PEAS.

Examination of fifteen cans of green peas was made and the results are given in Table 2.

In the case of peas neither shipment nor age seems to have had any appreciable effect, as the results are about the same throughout. There is very much less variation in all the determinations than in the determinations on the tomatoes. The average amount of fluid was 34.9 per cent, with a variation between 28.7 per cent and 38.6 per cent. The solids in the unfiltered fluid are rather erratic, while the solids in the filtered liquid are quite uniform. The refractometer reading is very uniform, varying between the narrow limits of 38.6 per cent and 42.8 per cent. The factor is also quite uniform.

RESULTS ON CANNED LIMA BEANS.

Examination of fifteen cans of lima beans was made corresponding to the fifteen cans of peas. In addition six cans of a rather miscellaneous lot of beans were examined, some having been soaked; the results ob-

TABLE 2.

Canned peas.

NO. OF SAMPLE	BRAND	LOCATION	Examined December, 1913: Liquid	Examined December, 1913: Specific gravity of liquid	Examined December, 1913: Solids in liquid	Examined December, 1913: Solids in filtered liquid	Examined December, 1913: Immersion refractive index of filtered liquid at 20°	Examined December, 1913: Polariscope reading (100 mm. tube)	Examined December, 1913: Factor: Refractive index divided by filtered solids	Shipped by express 2,000 miles and examined January, 1914: Liquid	Shipped by express 2,000 miles and examined January, 1914: Specific gravity of liquid	Shipped by express 2,000 miles and examined January, 1914: Solids in liquid	Shipped by express 2,000 miles and examined January, 1914: Solids in filtered liquid	Shipped by express 2,000 miles and examined January, 1914: Immersion refractive index of filtered liquid at 20°	Shipped by express 2,000 miles and examined January, 1914: Polariscope reading (100 mm. tube)	Shipped by express 2,000 miles and examined January, 1914: Factor: Refractive index divided by filtered solids	Kept in one place and examined July, 1914: Liquid	Kept in one place and examined July, 1914: Specific gravity of liquid	Kept in one place and examined July, 1914: Solids in liquid	Kept in one place and examined July, 1914: Solids in filtered liquid	Kept in one place and examined July, 1914: Immersion refractive index of filtered liquid at 20°	Kept in one place and examined July, 1914: Polariscope reading (100 mm. tube)	Kept in one place and examined July, 1914: Factor: Refractive Index divided by filtered solids
			per cent		*per cent*	*per cent*				*per cent*		*per cent*	*per cent*				*per cent*		*per cent*	*per cent*			
6171	May Duke	Rochester, N. Y.	35.63	1029	6.58	6.34	41.2		6.49	38.6	1031	7.20	6.46	41.0		6.34	34 9	1024	4.53	4.39	41.0	6.5	9.34
6171	May Duke	Rochester, N. Y.	37 81	1028	6.67	6.30	41.5		6.59	36.5	1030	7 57	7.06	42.8		6.06	37 8	1025	5 82	5 18	39.2	5.9	7.56
6171	May Duke	Rochester, N. Y.	38.00	1027	6.88	6.41	41.9		6.53	35.1	1031	7.24	6.81	42.3		6.21	35.5	1027	4 30	5 55	40.3	7.0	7.26
6214	Powhatan	Richmond, Va.	30.5	1032	8.55	6.53	41.5		6.35	34.6	1033	8.57	6.16	41.3		6.86	35 0	1030	7.06	5.46	38.6		6.81
6214	Powhatan	Richmond, Va.	34.6	1029	7.90	6.18	40.7		6.56	35.4	1039	10.08	6.33	42.3		6.68	35 2	1029	6.57	5.86	39.0		6.65
6214	Powhatan	Richmond, Va.	30.3	1035	9.82	6.40	41.4		6.47	28.7	1035	10.89	5.44	39.4		7 20	34.2	1030	7.17	5.98	39.7		6.65
		Average	34.5	1030	7.73	6.36	41.4		6.50	34.8	1033	8.58	6.38	41.5		6.56	35.4	1027	5.91	5.43	39.6		7 38
		General average								34.9	1030	7.30	6.06	40.8		6.81							

TABLE 3.

Canned lima beans.

NO. OF SAMPLE	BRAND	LOCATION	Examined December, 1913: Liquid	Examined December, 1913: Specific gravity of liquid	Examined December, 1913: Solids in liquid	Examined December, 1913: Solids in filtered liquid	Examined December, 1913: Immersion refractive index of filtered liquid at 20°	Examined December, 1913: Polariscope reading (100 mm. tube)	Examined December, 1913: Factor: Refractive index divided by filtered solids	Shipped by express 2,000 miles and examined January, 1914: Liquid	Shipped by express 2,000 miles and examined January, 1914: Specific gravity of liquid	Shipped by express 2,000 miles and examined January, 1914: Solids in liquid	Shipped by express 2,000 miles and examined January, 1914: Solids in filtered liquid	Shipped by express 2,000 miles and examined January, 1914: Immersion refractive index of filtered liquid at 20°	Shipped by express 2,000 miles and examined January, 1914: Polariscope reading (100 mm. tube)	Shipped by express 2,000 miles and examined January, 1914: Factor: Refractive index divided by filtered solids	Kept in one place and examined July, 1914: Liquid	Kept in one place and examined July, 1914: Specific gravity of liquid	Kept in one place and examined July, 1914: Solids in liquid	Kept in one place and examined July, 1914: Solids in filtered liquid	Kept in one place and examined July, 1914: Immersion refractive index of filtered liquid at 20°	Kept in one place and examined July, 1914: Polariscope reading (100 mm. tube)	Kept in one place and examined July, 1914: Factor: Refractive Index divided by filtered solids
6172	White Cap	Richmond, Va.	31.80	1030	5.96	5.57	38.5		6.91	30.7		5.34	4.90	34.7		7.08	36.1		4.67	4 44	34 7	1.8	7.81
6172	White Cap	Richmond, Va.	35.00	1027	5.39	5.09	36.8		7.23	38.1		5.55	4.81	34.8		7 23	29.1		4.33	4 23	33 4	1.5	7 89
6172	White Cap	Richmond, Va.	30.00	1031	5.98	5.51	38.0		6.89	37.0	1032	6.89	5.33	37.0		6.94	34.6		5.10	4 74	36.1	1.5	7.62
6215	Sona	Jersey City, N. J.	38.00	1039	10 27	7.22	45.2	3.4	6.26	41.9	104	10.93	6.51	42.3	2.0	6.49	35 2		10 70	7 21	43.6		6.04
6215	Sona	Jersey City, N. J.	34.6	1051	11.43	9.77	55.4	4.7	5.67	38.8	1048	11.70	8.96	52.5	4.1	5.86	46.1		8 45	6 87	42 2		6 14
6215	Sona	Jersey City, N. J.	32.3	1040	10.66	7.34	45.5	2.6	6.06	35.3	1050	12.36	7.53	45.7	2.1	6.07	39.4		10 28	7.00	42 2		6 00
		Average	33.6	1036	8 28	6.75	43.2		6.50	37.0	1043	8.79	6.34	41.1		6.30	36.9		7 25	5.75	38.7		6.91
		General average								35.8	1039	8.11	6.28	41.1		6.57							
6183	Monogram Butter Beans	Richmond, Va.	14.0			6.47	41.4	2.4	6.40														
6183	Monogram Butter Beans	Richmond, Va.	26.1		6.29	5.93	39.6		6.70														
6194	Boston Lima (Soaked)	Baltimore, Md.	33.0		10.51	8.18	48.2	4.2	5.90														
6194	Boston Lima (Soaked)	Baltimore, Md.	35.8		10.57	8.12	48.1	3.2	5.92														
6195	Soaked Lima	Baltimore, Md.	39.5		6.08	5.29	37.6	4.2	7.10														
6195	Soaked Lima	Baltimore, Md.	42.5		5.78	4.98	36.5	3.9	7.33														
		Average	31.8		7.85	6.50	41.9	3.6	6.56														

tained on these beans are given in Table 3 but not included in the general average.

The average amount of fluid was 35.8 per cent, with a variation between 30 per cent and 46.1 per cent. Shipment and age both seem to have had a slight effect in increasing the amount of fluid, but the increase is of little consequence. All of the results are quite wide apart, except the factor which is nearer a constant than in the case of the tomatoes and the peas. There were not enough brands of peas or beans examined to find out just how variable the results would be. The contents of all of the cans examined were in good condition, and we believe honestly packed.

GENERAL CONCLUSIONS.

(1) Shipment does not seem to have any appreciable effect on the amount of fluid of canned tomatoes and green peas and a very slight effect on the amount of fluid of lima beans.

(2) Age seems to increase the amount of fluid in canned tomatoes and lima beans very slightly, but hardly at all in canned green peas.

(3) The per cent of easily-separable fluid is a very poor index of the character of canned tomatoes, peas, or lima beans.

(4) The refraction index is probably the best index of the character of the fluid in all canned goods.

A paper on the "Characteristics of Common and Lima Beans" was read by Arno Viehoever of the Bureau of Chemistry.

REPORT ON COCOA AND COCOA PRODUCTS.

By H. C. Lythgoe (State Department of Health, Boston, Mass.), *Associate Referee.*

At the meeting two years ago the Baier and Neumann method for the determination of casein was recommended for provisional adoption by Mr. Dubois, associate referee. At the meeting last year the present associate referee recommended the method for final adoption as provisional. Objection was made to this method by Mr. Dubois because he had found a sample alleged to be milk chocolate which gave no reaction for casein by the above method, but which contained the proper proportion of butter fat and milk sugar. According to information received from the manufacturer, this chocolate was made by a method somewhat different from that usually employed, and the committee on recommendations recommended further study upon the method before adoption as provisional. In conversation with Mr. Dubois he stated, in answer to a direct question, that the department had no knowledge whether or not the manufacturer used butter and glucose to simulate the chemical com-

position of milk chocolate, but a very careful survey of the factory made after the manufacturer was given a hearing gave no indication that such was the practice.

The Bureau of Chemistry intended to make a study of the condition under which this particular milk chocolate was manufactured and samples of the product were to be forwarded to the associate referee. No samples have been received to date and on October 28 I learned from Mr. Dubois that the investigation had been dropped by the Bureau.

The associate referee has used this method for several years, not only for the determination of casein in milk chocolate, but also in other food products in which milk or casein is used as an ingredient, and has never experienced any trouble with it, but considering the objections given by Mr. Dubois, does not consider it advisable that the method be adopted at present as provisional.

For the past three years the method of Ulrich[1] for the determination of cocoa red has been used in the Laboratory of Food and Drug Inspection of the Massachusetts State Board of Health for the detection of added shells. This method possesses no material advantages over the determination of pentosans or of fiber for this purpose, but as the product determined is a constituent of the cocoa nibs and is absent in the shell, while the pentosans and fiber are constituents of the shells and not of the nibs, the determination may be of interest to the association. The method is as follows:

To 1 gram of fat-free dry substance, which should be finely powdered, in a 300 cc. Erlenmeyer flask, add 120 cc. of pure acetic acid (50 to 51 per cent); connect with a return-flow condenser and boil for 3 hours; cool and bring the contents of the flask to a volume of 150 cc. with cold water; shake well and allow to stand at least 12 hours; filter through a dry filter and treat 135 cc. of the filtrate (corresponding to 0.9 gram of the original substance) with 5 cc. of concentrated hydrochloric acid and 20 cc. of a 20 per cent ferric chlorid solution. Connect with a return-flow condenser, heat to the boiling point and boil 10 minutes; cool quickly and transfer to a beaker; after letting stand at least 6 hours, filter upon a weighed filter, washing the precipitate with hot water until free from iron; dry for 6 hours at 105° C. and weigh.

Results of analyses of 18 samples of commercial cocoa.

(Per cent.)

	MOISTURE	FAT	FAT-FREE SUBSTANCE			COCOA RED
			Ash	Fiber	Pentosans	
Highest	4.80	25.07	7.78	8.32	4.55	16.22
Lowest	2.60	15.07	5.80	5.33	3.97	11.17
Average	3.87	19.95	6.58	6.35	4.44	14.06
Dutch process, average	4.76	24.37	9.87	6.24	4.47	13.47

[1] Der Nachweis von Schalen im Kakao und in seinen Preparaten von Diplom-Ingeneur Chrostoph Ulrich. Dissertation, Detmold 1911.

The examination of 41 samples of commercial cocoa in 1914 gave from 11.22 to 17 per cent, average 15.17 per cent of cocoa red. Ulrich reports for different varieties of cocoa nibs averages from 11.12 per cent to 16.54 per cent.

RECOMMENDATION.

It is recommended—

That the associate referee on cocoa products for the year 1915 make a study of the manufacture of milk chocolate with the view of finding out whether or not the casein is rendered insoluble in the reagents by different methods of manufacture.

REPORT ON TEA AND COFFEE.

By J. M. Bartlett (Agricultural Experiment Station, Orono, Me.), *Associate Referee.*[1]

According to the recommendations adopted by the association at its last meeting the work on tea and coffee has been confined to methods for the determination of caffein.

One sample each of tea and coffee was sent out to all chemists signifying a desire to coöperate in the work, together with the following instructions:

INSTRUCTIONS TO COLLABORATORS.

Determine caffein or thein in each of the samples by the following methods:

Method 1.—Carefully weigh 10 grams in No. 60 powder into a 500 cc. Erlenmeyer, add 100 cc. of water and 10 cc. of 10 per cent hydrochloric acid and heat to boiling with reflex condenser for 2 hours. Cool, decant liquid through a filter, treat solid material with 3 portions of 50 cc. each of boiling water, filtering through same paper as above and then wash material on filter with 50 cc. of boiling water. Concentrate to 150 cc. by evaporating over steam or water bath. Transfer filtrate to a 500 cc. separator, Squibb type, add 5 cc. of stronger ammonium hydroxid, shake out with 50 cc. portions of chloroform five times. After the first shaking out let the separator rest until separation is as complete as it will be; then run chloroform into another 500 cc. separator; add the second portion of chloroform and shake again, after standing until no further separation occurs, run the solvent and the adhering emulsion, if any, into the second separator but do not run in any of the non-emulsified liquid. Repeat three times, running chloroform and any emulsion into the second separator. Then discard the liquid in the first separator and give a second separator containing the chloroform and emulsion a violent shaking; let stand and then run chloroform into a 250 cc. Erlenmeyer flask. If there is an emulsion remaining in the separator, add 1 to 5 cc. of 94 per cent alcohol and shake. When the chloroform has separated add it to that in the 250 cc. flask. Add about 25 cc. of chloroform to the aqueous alcoholic layer in the separator and agitate; after separation run the chloroform into the 250 cc. flask and then evaporate off the chloroform on the steam bath using a moderate blast of air and removing from bath as last portions evaporate to avoid

[1] Read by H. H. Hanson.

spattering. When the residue of crude caffein is dry, add 10 cc. of dilute 10 per cent hydrochloric acid and 50 cc. of water and warm until caffein is dissolved. Cool and precipitate with 50 cc. of iodin solution (10 grams of iodin, 20 grams of potassium iodid, 100 cc. of water), stopper flask with cork and let stand overnight.

Filter through 9 cm. filter and refilter filtrate, if necessary, washing flask and precipitate twice with iodin solution, but not attempting to remove all of the precipitate from the flask. Transfer filters to flask in which precipitation was made, add 0.5 gram of sodium acid sulphite or sodium sulphite, 3 cc. of 10 per cent sulphuric acid and 15 cc. of water and warm until iodid is decomposed, more salt being added if the amount is insufficient to decolorize.

Filter into a separator (small 100 cc.), add excess ammonium hydroxid stronger and shake out five times with 15 cc. portions of chlorform. Wash the combined chloroform extracts with water which is discarded and then concentrated to 10 to 15 cc. add dry animal charcoal, shake and allow to stand 1 hour with occasional shaking, filter through a small filter into a tared dish, washing flask and filter three or four times with 5 cc. portions of chloroform. Evaporate chloroform and dry residue in a desiccator and weigh.

Method 2 (*Gorter method for coffee*).—Moisten 11 grams of finely-powdered coffee with 3 cc. of water, allow to stand for half an hour, and extract for 3 hours in a Soxhlet extractor with chloroform. Evaporate the extract, treat residue of fat and caffein with hot water, filter through a cotton plug and moisten filter paper, and wash with hot water. Make up the filtrate and washings to 55 cc., pipette off 50 cc. and extract four times with chloroform. Evaporate this chloroform extract in a tared flask and dry the caffein at 100° C. and weigh. Transfer residue to Kjeldahl flask with a small amount of hot water and determine nitrogen by Kjeldahl or Gunning method. Nitrogen multiplied by 3.464 equals caffein.

It is suggested that after shaking out the aqueous solution with chloroform, run the chloroform into a second separator and shake with a strong solution of sodium carbonate. The sodium carbonate solution will remove most of the coloring matter. Then pass the chloroform to a third separator and wash with water. Treat the remaining chloroform shakeouts from the aqueous solution in the same manner, passing them successively through the sodium carbonate and wash water.

The washed chloroform extracts are then united, evaporated, dried and weighed.

Method 3 (*Modification of Stahlschmidt's method for tea*).—Boil 6 grams of finely-powdered tea in a flask with several successive portions of water for 10 minutes each, and make up the combined aqueous extracts thus obtained to about 550 cc. with water. Add 4 grams of powdered lead acetate to the decoction, then boil for 10 minutes, using a reflux condenser; add water so that the solution will finally be exactly 600 cc., and cool to room temperature. Then pour the solution upon a dry filter and evaporate 500 cc. of the filtrate, corresponding to 5 grams of the tea, to about 50 cc., and add enough sodium phosphate to precipitate the remaining lead. Filter the solution, and thoroughly wash the precipitate, the filtrate and washings being evaporated to about 40 cc. Finally extract the solution thus concentrated with chloroform in a separatory funnel at least four times and evaporate the chloroform extract to dryness, leaving the caffein, which is dried to constant weight at 75° C. and weighed.

RESULTS REPORTED BY COLLABORATORS.

Reports were received from only two collaborators; therefore, only a few results are given in the following table:

Results obtained on tea and coffee.

SAMPLE AND ANALYST	METHOD	CAFFEIN	
		Weighed	Calculated from nitrogen
		per cent	*per cent*
TEA:			
H. H. Hanson, Orono, Me.	No. 1. Fuller	2.70	....
	No. 3. Stahlschmidt	3.09	2.74
	New method	3.38	2.81
H. C. Fuller, Institute of Industrial Research, Washington, D. C.	No. 1. Fuller	2.47	....
	No. 3. Stahlschmidt	2.61	....
COFFEE:			
H. H. Hanson	No. 1. Fuller	1.28	....
	No. 2. Gorter	1.36	1.04
	New method	1 24	1.25
H. C. Fuller	No. 1. Fuller	1.12	....
	No. 2. Gorter	1.06	....

COMMENTS OF COLLABORATORS.

H. H. Hanson: In preparing the tea or coffee for work we have found that the recommendation to grind the materials so as to pass a sixty-mesh sieve not necessary, and, in the case of coffee, rather impractical. Upon samples ground to pass a forty-mesh sieve exactly as good results were obtained, and, in the case of coffee, better results.

With the Fuller method good results were apparently obtained with both tea and coffee, but it is a long and involved one, and, while apparently accurate, is time-consuming and involves very careful manipulation.

The Stahlschmidt method for tea is apparently quite correct if the result obtained by weighing is not taken as a final result, but a nitrogen determination made upon this result and the caffein calculated from the nitrogen content.

The Gorter method for coffee is apparently only approximately correct.

In reporting the results obtained on tea and coffee I wish to call attention to a new or combined method which has in our laboratory seemed to work out very well. This new method, besides the three given by the associate referee, has been carefully studied. The results reported are only those obtained after the methods had been tried once, so that the analyst was familiar with the method.

The new method gave good results with both tea and coffee almost without exception. Some difficulty was experienced in first trying out the method with tea. In the mind of the analyst the new method is as accurate and considerably more rapid than the Fuller method for coffee, and the Stahlschmidt method with the modification mentioned is the quickest and most accurate method for tea, but only slightly more rapid than the new method. The new method, which is given below in detail, is taken in part from the other three methods.

Place 5 grams of material in an extraction thimble and moisten with 5 to 7 cc. of water, and allow to stand for about 30 minutes. Place a loose cotton plug in the top of the thimble and extract with chloroform in a Soxhlet extractor for at least 3 hours. Evaporate off most of the chloroform and add 10 cc. of 10 per cent hydrochloric acid and 50 cc. of water, and heat to boiling to dissolve caffein. Cool, precipitate caffein with iodin solution as in the Fuller method, the solution being made with 10

grams of iodin, 20 grams of potassium iodid and 100 cc. of water. Use 25 cc. of this solution for the precipitation, cork the flask, and allow to stand overnight. Filter this on a small filter paper (9 cc. is about right) and wash with some of the solution. Transfer the filter paper and contents back to the flask in which the precipitation was made, add 0.5 gram of sodium acid sulphite or sodium sulphite with 3 cc. of 10 per cent sulphuric acid and about 15 cc. of water. Warm this until the iodid is decomposed, cool, dilute, make ammoniacal and then make up to the mark. Filter through a dry filter and take a 50 cc. portion for the extraction, which is made with chloroform, using about 5 portions of 15 to 25 cc. each. Evaporate off the chloroform and determine the nitrogen. The nitrogen content multiplied by the factor 3.464 gives the caffein.

Results obtained on tea and coffee.

(Per cent.)

SAMPLE AND METHOD	FINENESS OF SAMPLE	RESULTS	
		Weighed	Calculated from nitrogen
TEA:			
Fuller	20-mesh	2.71	....
Fuller	60-mesh	2.68	....
Stahlschmidt	60-mesh	3.08	2.67
Stahlschmidt	60-mesh	3.10	2.81
New method	60-mesh	3.38	2.77
COFFEE:			
Fuller	40-mesh	1.28	....
Gorter	40-mesh	1.38	1.11
Gorter	40-mesh	1.34	0.96
New method	40-mesh	1.24	1.25

H. C. Fuller: You will note that I have sent no figures for the Kjeldahl determination of nitrogen, for the reason that the total caffein obtained was less than that found by Method 1.

DISCUSSION.

So few analysts have taken part in the work this year that the associate referee does not think the methods have been sufficiently tested to warrant recommending either of them as an official method. Only a few members of the association are particularly interested in this kind of work, consequently it is difficult to get much coöperation. It is very desirable, however, that the association have an official method for the determination of this important constituent of tea and coffee. The Gorter and Stahlschmidt methods, slightly modified, in the hands of experienced men give quite closely agreeing results. The Fuller method, which is applicable to both tea and coffee, also gives good results, but the first part of the process is tedious and difficult to carry through satisfactorily. The combination method suggested by Mr. Hanson using the Gorter method of extraction and Fuller method of purification appears to give good results and I think is worthy of our consideration.

RECOMMENDATION.

It is recommended—

That the associate referee on tea and coffee for next year continue the study of methods for the determination of caffein in tea and coffee and that the combination method suggested by Mr. Hanson in this report be given a trial.

REPORT ON PRESERVATIVES.

By A. F. Seeker (Bureau of Chemistry Food and Drug Inspection Laboratory, New York, N. Y.), *Associate Referee.*

Following the plan recommended at the last meeting a further study has been made of the Fincke method for the determination of formic acid, together with a trial of the Fenton and Sisson reduction of formic acid to formaldehyde as a qualitative means for the detection of the preservative in foods. The coöperative work of last year having shown the Fincke method to be sufficiently accurate as a general means for the determination of formic acid, the endeavor during the present year has been to ascertain what effect various possible interfering substances may have upon its accuracy and also to determine how much formic acid various natural and prepared food products may normally appear to contain when examined by the prescribed method.

The possible interfering substances that have been suggested (Biochem. Zts., 1913, **51:** 253) are sorbic, levulinic, glyoxylic, cinnamic, fumaric, salicylic and benzoic acids. In the work tabulated in Table 1 the levulinic, cinnamic and fumaric acids used were of Kahlbaum's, the salicylic and benzoic of Merck's manufacture, the effect of sorbic and glyoxylic acid being studied by determinations conducted upon the fruits in which these two acids occur naturally, these being respectively unripe sorb apples and unripe gooseberries.

The gooseberries selected for this purpose were purchased from local dealers. The sorb apples were secured through the courtesy of H. H. Rusby from the Bronx Botanical Gardens, New York City, from trees grown at that institution. The trees were of the European species, *Sorbus Aucuparia,* L., known in England as the mountain ash or service tree, and in Germany as the Eberesche or Vogelbeere. The juice of the fruit is used to some extent in the preparation of German and Hungarian cordials.

In the above work (1) was conducted by adding the levulinic acid to 50 cc. of lime juice that had just been subjected to steam distillation for the determination of formic acid, and going through the procedure in the regular way. (3), (4), (6), (8) and (10) were conducted by dissolving the

TABLE 1.

Amount of precipitate expressed as formic acid obtained in the Fincke method when applied to certain possible interfering substances.

SUBSTANCE	AMOUNT EMPLOYED	EQUIVALENT OF FORMIC ACID
	grams	*mg.*
(1) Levulinic acid	0.5	1.5
(2) do	0.5	0.4
(3) do	2.0	0.6
(4) Cinnamic acid	0.1	None
(5) do	0.2	0.4
(6) Fumaric acid	0.1	0.3
(7) do	0.2	0.4
(8) Salicylic acid	0.1	None
(9) do	0.2	0.4
(10) Benzoic acid	0.1	None
(11) do	0.2	None
(12) Unripe sorb apples (very green)	25.0	1.5
(13) do	25.0	0.6
(14) Unripe sorb apples (almost mature)	50.0	0.5
(15) do	50.0	0.5
(16) Ripe sorb apples	50.0	0.5
(17) Unripe gooseberries	50.0	2.0
(18) do	50.0	1.1
(19) do	50.0	2.1

respective substances in 150 cc. of water, treating with 2 grams of barium carbonate, heating to boiling, filtering while hot, and subjecting to the mercuric chlorid treatment in the regular way. In all the other determinations the substances were dissolved or suspended in 50 or 100 cc. of water and subjected to all the operations of the regular procedure.

It will be seen from Table 1 that the interference of all the substances mentioned is negligible being well within the limits of accidental error. The identity of the levulinic acid was verified by preparing the silver salt and determination of the contained silver. Melting points were determined upon the other pure acids used excepting fumaric which behaved in its characteristic manner when heated to 286° to 290°, subliming without perfectly liquifying.

As noted in the last report substances containing considerable amounts of caramelized carbohydrates give results indicating the presence of appreciable quantities of formic acid. This has been verified by determining formic acid in infusions of five samples of roasted coffee of known history. The infusions were prepared by boiling 100 grams of ground coffee with 500 to 600 cc. of water, filtering, washing with hot water, boiling down the filtrate and washings to about 100 cc., and conducting the determination upon this extract. They yielded the equivalent of 60, 43, 72, 109 and 111 mg. of formic acid respectively, the identity and amount of formic acid being verified in the last two cases by the carbon monoxid method of Wegner, the gas evolved representing 0.115 and 0.123

per cent, respectively. A sample of roasted chicory gave 48 mg. of formic acid by the Fincke method. Two samples of commercial caramel used for coloring purposes gave respectively 602 and 236 mg. of formic acid per 100 grams. Three samples of cocoa gave respectively 22, 30, and 18 mg. of formic acid per 100 grams. In order to ascertain whether preparations containing highly-roasted cereal may appear to contain formic acid from this source, several very dark beers were subjected to the procedure with results indicated below:

SERIAL NO.	PRODUCT	MERCURIC CHLORID REDUCTION EQUIVALENT TO MG. OF FORMIC ACID
		mg. per 100 cc.
N. Y. 48771	Guiness' Stout Extra	2.2
48662	La Tropica, Dark Beer	1.5
48717	Bass' Dog's Head Ale	1.0
48584	Sparkling English Ale	1.0
44283	Kop's Dark Imitation Beer (non-alcoholic)	4.1

Except in the caramel itself or in a highly-roasted solid like coffee the amount of formic acid from caramelized carbohydrates as determined by this method appears to be negligible. It may be mentioned in this connection that in case the substance under examination is overheated in the course of the distillation and the sugars more or less caramelized the results are certain to be too high. An instance of this was mentioned in the last report and for the sake of comparison is again given together with two more recent cases.

SUBSTANCE	CARAMELIZED DURING DISTILLATION	PROPERLY DISTILLED
	per cent formic acid	*per cent formic acid*
Grape jelly	0.028	0.008
Cherry jam	0.085	0.006
Strawberry jam	0.064	0.005

As a further possibility of formic acid appearing to arise in food products through the agency of natural processes the statement of Kingzett and Woodcock[1] was considered, in which it is said that the slow oxidation of terpenes in the presence of moisture produce the preservative. Into each of four bottles 200 cc. of water were introduced and this covered with 5 cc. of lemon oil, the neck of the bottle being closed with a loose cotton plug. The bottles were allowed to stand in a dark closet, three for 12 months and one for 16 months the contents being occasionally shaken during

[1] Chem. News, 1912, **105**: 26; J. Soc. Chem. Ind., 1910, **29**: 791.

these periods. At the end of the time an excess of magnesium carbonate was added and the mixture filtered. Formic acid was determined by Fincke's method in 100 cc. of the clear filtrate. The amount of formic acid found per 100 cc. of filtrate was as follows: In the 12-month experiment, 21.2, 28.9, 22.5 mg.; in the 16-month experiment, 35.2 mg.

During the year a number of commercial products as well as some fruit juices pressed by the referee were examined by the method with a view toward ascertaining how much mercuric chlorid is ordinarily reduced by different products free from added formic acid. The results are tabulated.

TABLE 2.

Analysis of fruit juices and commercial products.

SERIAL NO.	SUBSTANCE	MERCURIC CHLORID REDUCTION EXPRESSED AS FORMIC ACID
		per cent
....	Apricot juice[1]	0.001
....	Strawberry juice[1]	0.003
....	Gooseberry juice[1]	0.003
....	Raspberry juice[1]	0.004
....	Blackberry juice[1]	0.003
....	Cherry juice[1]	0.004
....	Peach juice[1]	0.002
....	Pineapple juice[1]	0.006
....	Apple juice[1]	0.005
....	Apple juice[1]	0.006
N. Y. 42677	Pineapple juice, Cuban	0.007
43099	Strawberry liqueur	0.003
43100	Cherry sirup	0.006
44291	Cranberry jam	0.018
44702	Orange pulp	0.002
45595	Lime juice	0.001
47072	Plum jam	0.005
45583	Raspberry sirup	0.005
45623	Blackberry cordial	0.003
45859	Red currant jelly	0.007
45860	Raspberry and currant jam	0.004
45861	Raspberry jam	0.011
46560	Cider	0.002
46134	Wild bramble and apple jelly	0.004
46133	Orange marmalade	0.003
46826	Raspberry sirup	0.006
46827	Strawberry sirup	0.008
46831	Lime juice	0.005
47009	Lime juice cordial (contained salicylic acid)	0.006
46927	Currant jelly	0.013
47527	Strawberry juice	0.004
47652	Lemon juice	0.003
47918	Apricot pulp	0.004
48076	Cherry cordial	0.008
48213	Pineapple sirup	0.005
48331	Raspberry sirup	0.006
48332	Raspberry sirup	0.005
48720	Pineapple pulp (Straits Settlements)	0.005
49009	Apricot pulp	0.006
49012	Raspberry jam	0.007

[1] Pressed by associate referee.

TABLE 2.—*Continued.*

Analysis of fruit juices and commercial products.

SERIAL NO.	SUBSTANCE	MERCURIC CHLORID REDUCTION EXPRESSED AS FORMIC ACID
		per cent
49013	Strawberry jam	0.008
49014	Black currant jam	0.008
49105	Cherry jam	0.004
49106	Strawberry jam	0.009
49107	Raspberry jam	0.007
49147	Strawberry jam	0.010
49195	Apricot pulp	0.006
49198	Apricot pulp	0.004
49221	Pineapple pulp (Straits Settlements)	0.007
49298	Pineapple pulp (Straits Settlements)	0.004
49521	Strawberry pulp	0.003
Various	Eighteen samples of honey from Cuba, Santo Domingo and Mexico varied between	0.002 and 0.016

Among the miscellaneous samples examined were a Russian caviar (0.011 per cent formic acid), two samples of English table sauces (0.021 and 0,011 per cent), and a Japanese sake (0.001 per cent). The referee wishes to express his acknowledgments to M. G. Wolf of the New York Food and Drug Inspection Laboratory to whom credit is due for the examination of a large part of the commercial samples here given.

The fact that honey naturally contains little or no formic acid is further established by the recently-published work[1] of several authors who have examined authentic samples and found between 0.001 and 0.028 per cent.

During the past year five fruit products of foreign origin have been found to contain added formic acid. The amounts found ranged between 0.03 and 0.25 per cent. The products consisted of two raspberry sirups, a black currant sirup, an elderberry sirup, and a cranberry juice. In one case the manufacturer furnished the information that 0.05 per cent of formic acid had been added to his product. The amount found was 0.041 per cent which accords well with his statement when it is considered that the acid used by the manufacturer was probably not absolute but of a concentration ranging between 60 and 80 per cent.

The results of experimental work upon a practical qualitative test for formic acid have proved somewhat unsatisfactory. A practical qualitative test should give an absolutely negative indication in the absence of added formic acid. The reduction of the formic acid in the steam distillate of food products by means of magnesium ribbon according to the

[1] Ber. d. Nahr. Unters., Bromberg, 1912, v. 20: Jahresber. d. Nahr.-Unters. Landwirtschaftskammer für Brandenburg, Berlin und Frankfort a. O., 1912, v. 34: Jahresber. d. Nahr. Unters., Kiel, 1912, v. 16: Jahresber. d. Chem. Unter. Hannover, 1912, v. 18.

method proposed by Fincke and given in detail in the associate referee's previous report was found in this year's work to give a slight positive test in a number of samples of natural products in which added formic acid was known to be absent. It is true that when added formic acid amounting to about 0.1 per cent or more was present the test became decidedly stronger and to an experienced worker the results probably would not prove misleading. The associate referee does not feel that it ought to be recommended as a general test. The tests proposed by Shannon[1] are excellent and reliable. They are based upon four characteristics of formic acid: Its volatility with steam, the crystal form of its lead salt, the formation of carbon monoxid when heated with concentrated sulphuric acid, and its reducing power. Two of these characteristics are employed in the Fincke quantitative method with less consumption of time and with the added information of quantity. The crystallographic recognition requires special knowledge, but the formation of carbon monoxid taken together with the results of the Fincke determination is sufficient and convincing proof. While Shannon's method is excellent for obtaining this test the Wegner procedure[2] is perhaps to be preferred because with about the same amount of manipulation and time quantitative results are obtained. Working with the apparatus recommended by Röhrig[3] the associate referee obtained the following results upon two pure fruit juices containing known amounts of formic acid:

Formic acid in pure juices.

SUBSTANCE	AMOUNT ADDED	AMOUNT FOUND BY FINCKE METHOD	AMOUNT FOUND BY ROHRIG METHOD
Strawberry juice..........	0.0992	0.0941	0.0982
do	0.0496	0.0465	0.0500

RECOMMENDATIONS.

In view of the excellent results obtained by the collaborators with the Fincke method last year and considering the results of the examination of the varied commercial and natural products during the present year, it is recommended that the Fincke method be adopted as a provisional method by the association, with all the details as given in the report of last year.

It is also recommended that the Wegner method be submitted to trial as a confirmatory test, and that steps be taken to secure a reliable quantitative method for the determination of saccharin in foods.

No report was made by the referee on water in foods and feeding stuffs.

[1] J. Ind. Eng. Chem., 1912, **4**: 526.
[2] Zts. anal. Chem., 1903, **42**: 427.
[3] Zts. Nahr. Genussm., 1910, **19**: 4.

REPORT ON INORGANIC PHOSPHORUS IN ANIMAL AND VEGETABLE SUBSTANCES.

By E. B. Forbes, *Referee*, and F. M. Beegle (Agricultural Experiment Station, Wooster, Ohio).

INORGANIC PHOSPHORUS ESTIMATION IN ANIMAL TISSUES.

In previous referee work on inorganic phosphorus estimation in animal tissues three methods have been compared, namely, the neutral molybdate method of Emmett and Grindley, the modified barium chlorid method of Siegfried and Singewald, and the magnesia mixture method of Forbes and associates. Satisfactory comparisons of these methods have been made on muscle, the results being practically identical; and certain important limitations to the applicability of the two methods first mentioned, to tissues other than muscle, have been established. It was now desired to test, by the method of recovery of added phosphates, the accuracy of the magnesia mixture method, in its latest form, with animal tissues of diverse character, and also to study individually, a number of details of this method, as: (1) The influence of heat, as specified; (2) the method of filtration; (3) the completeness of extraction; (4) the influence of ammonium sulphate, as specified; (5) the effects of varying amounts of ammonium sulphate; and (6) different methods of use of ammonium sulphate.

In the test of the accuracy of the magnesia mixture method, determinations were made, in triplicate, on blood, brain, flesh, and liver, with and without the addition of known amounts of inorganic phosphate. The detailed directions followed in this test are on pages 562 to 565, and the results are set forth in Table 1. The results of the further analytical proving of the details of the method were all made on blood. The data are to be found in Tables 2 to 5.

PREPARATION OF COLD WATER EXTRACT OF MUSCLE.

A. COLD WATER EXTRACT OF MUSCLE.

Weigh out 10 to 12 grams of fresh muscle, and divide as nearly equally as possible between two small beakers. Moisten the samples with a few cubic centimeters of distilled water, and break up lumps with a glass rod. Add 50 cc. of water to each beaker and stir contents for 15 minutes. Allow insoluble residue to settle for 3 to 5 minutes; then decant the liquid from each beaker through filters into beakers; allow to drain and add 25 cc. of distilled water. Stir for 7 to 8 minutes, and after allowing to settle, decant onto the same filter. Continue this treatment, using each time 25 cc. of water, until the filtrates measure about 230 cc. each. Allow the filters to drain completely between extractions. Whenever the major portion of the residue has become mechanically transferred to the filter, return it to the beaker, using great care not to break the filter paper. After the last extraction throw the entire

contents of each beaker onto the filter, and, when drained, wash twice with small quantities of distilled water. Combine the two extracts, and use for the precipitation of the phosphates as described on page 565.

B. COLD WATER EXTRACT OF MUSCLE PLUS PHOSPHATE.

Weigh out 10 to 12 grams of flesh, and divide as nearly equally as possible between two small beakers; work up with a few cubic centimeters of distilled water; add 25 cc. of aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate dividing as nearly equally as possible between the two beakers and proceed as directed under A. The extract thus obtained is ready for precipitation as described on page 565.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BLOOD.

A. HOT WATER AMMONIUM SULPHATE EXTRACT OF BLOOD.

Weigh out 30 to 35 grams of fresh blood (entire portions as caught from the animal) into a porcelain mortar. Grind and transfer to a 400 cc. beaker with hot distilled water, make up to about 150 cc. with boiling distilled water, place over a flame, and gradually bring to boiling, with constant stirring; when boiling begins add 20 cc. of 20 per cent ammonium sulphate solution, boil, with constant stirring, for about 10 minutes, decant onto an 18 cm. filter paper, receiving the filtrate in an 800 cc. beaker. When the liquid is through, lift the coagulum from the paper, being very careful to not break the paper filter, and transfer it, along with that remaining in the beaker, to the mortar. Grind to a smooth paste and transfer from mortar to beaker with boiling $3\frac{1}{3}$ per cent ammonium sulphate. Make up to about 50 cc. with the same, stir for 8 minutes, and pour contents again onto the filter paper. After the extract is through, return the coagulum to the mortar and grind a second time, transferring to the beaker as before with boiling $3\frac{1}{3}$ per cent ammonium sulphate. Repeat this process of 8-minute extractions of the coagulum in $3\frac{1}{3}$ per cent ammonium sulphate, and filtration as just directed, without further grinding, until the filtrate measures about 450 cc. Wash out each beaker twice with 8 to 10 cc. of hot $3\frac{1}{3}$ per cent ammonium sulphate, completing the transfer of the coagulum and extract to the filter paper. Wash the coagulum on the paper twice with boiling $3\frac{1}{3}$ per cent ammonium sulphate from a wash bottle. At all times allow the filter to drain well between additions of extract or wash solution. This extract of about 500 cc. is ready for precipitation as described on page 565.

B. HOT WATER AMMONIUM SULPHATE EXTRACT OF BLOOD PLUS PHOSPHATE.

Weigh out similar quantities of blood, grind in a mortar, and transfer to a beaker as specified in A. Add 25 cc. of an aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate and proceed as directed under A. The extract of about 500 cc. is ready for precipitation as directed on page 565.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF LIVER.

A. HOT WATER AMMONIUM SULPHATE EXTRACT OF LIVER.

Weigh by difference from closed weighing bottles 15 to 20 gram portions of finely ground liver into 400 cc. beakers. Add a few cubic centimeters of cold distilled water, and beat up with a stirring rod to separate the particles of tissue. Add enough

boiling distilled water to make the volume up to 150 cc.; place over a flame and bring to boiling. Add 10 cc. of 20 per cent ammonium sulphate and continue to boil for 10 minutes. Remove from the flame, allow to settle for a moment and decant the boiling-hot liquid onto 18 cm. paper filters. Add 50 cc. of boiling water and stir for 8 minutes, without further heating over a flame, and decant onto the filter again. Repeat this addition of 50 cc. of hot distilled water, stirring, and decanting eight times, returning the coagulum to the beaker as soon as any considerable amount collects on the filter. With the eighth portion of water throw the entire contents of the beaker onto the filter and wash twice with hot water from a wash bottle. At all times allow the filter to drain well between additions of extract or wash water. This extract of about 600 cc. is now ready for precipitation as described on page 565.

B. HOT WATER AMMONIUM SULPHATE EXTRACT OF LIVER PLUS PHOSPHATE.

Weigh out portions of liver as specified above. Work up with a few cubic centimeters of cold distilled water; add 25 cc. of an aqueous solution of disodium phosphate, equivalent to about 40 mg. of magnesium pyrophosphate and proceed as directed under A. The extract of about 600 cc. is ready for precipitation as directed on page 565.

PREPARATION OF HOT WATER AMMONIUM SULPHATE EXTRACT OF BRAIN.

A. EXTRACTION OF BRAIN.

Weigh out about 10 grams of brain into a 250 cc. beaker. Add a few cubic centimeters of distilled water, and work up the brain and water with a glass rod. Make up to about 100 cc. with boiling water; place over a flame, and gradually bring to boiling, with constant stirring. While boiling vigorously (not before) add 20 cc. of 20 per cent ammonium sulphate solution; boil gently for about 10 minutes; allow to settle for a moment, and decant liquid slowly onto a filter of sand on linen, receiving the extract in an 800 cc. beaker. Add to the beaker containing the coagulum 50 cc. of a $3\frac{1}{3}$ per cent ammonium sulphate solution, stir for 1 minute, keeping over flame and at the boiling point; decant the liquid onto the filter. Repeat this process of one-minute extractions of the coagulum in $3\frac{1}{3}$ per cent ammonium sulphate solution, and filtration as just directed, until the filtrate measures about 450 cc. Wash out the beaker twice with 8 to 10 cc. of hot $3\frac{1}{3}$ per cent ammonium sulphate solution, completing the transfer of the coagulum and extract to the sand. Wash the coagulum twice with the above wash solution from a wash bottle. At all times allow the filter to drain well between additions of extract or wash solution.

This extract of about 500 cc. is ready for precipitation as directed on page 565.

B. EXTRACTION OF BRAIN PLUS PHOSPHATE.

Weigh out about 10 grams of brain; work up with a few cubic centimeters of distilled water, add 25 cc. of an aqueous solution of disodium phosphate equivalent to about 40 mg. of magnesium pyrophosphate and proceed as directed under A. The extract thus obtained is ready for precipitation as described on page 565.

PRECAUTIONS.

In making extracts of brain it is desirable that the analyst give careful attention to the handling of the sample. The coagulum is very soft. It should be stirred only enough to keep it in motion. If roughly handled in returning from the sand

filter to the beaker it becomes too much broken up and holds onto a great deal of liquid. To prevent the extract or the coagulum from coming into contact with the linen before passing through the sand, pour the extract slowly into a slight depression in the center of the sand, or, better yet, onto a thin film of absorbent cotton 1½ inches in diameter, laid over a depression in the sand. The coagulum remains on the cotton, and its return to the beaker is thereby much facilitated. If the cotton is not broken up by needless stirring it can be taken out of the beaker with a glass rod and returned to the sand each time a partial extract is to be filtered. Care is necessary to prevent loss through bumping, on account of sand in the beakers during the last extractions. Three determinations at a time are enough for one man to handle, but, with some risk of loss, one can handle six. Each partial extract should be boiling hot at the time filtration begins.

MAGNESIA MIXTURE METHOD FOR THE DETERMINATION OF INORGANIC PHOSPHORUS IN EXTRACTS OF ANIMAL TISSUES.

Treat three of the extracts prepared according to the directions on the preceding pages according to Section A and three of those prepared according to Section B as follows:

Add 50 cc. of magnesia mixture, stirring freely; allow to stand 15 minutes; add 25 cc. of ammonia (specific gravity 0.90); cover, and allow to stand 3 days. On the morning of the third day filter, and wash the precipitate with 2.5 per cent ammonia water. Dissolve the precipitate on the filter paper and that remaining in the beaker in which the precipitation was made with dilute nitric acid (1:1) and hot water, receiving the solution in 400 cc. beakers. Neutralize the nitric acid with ammonia; make slightly acid with nitric acid. Add 5 grams of ammonium nitrate, and precipitate in the usual way with molybdate solution. Continue in the usual way for the gravimetric estimation of phosphorus as the pyrophosphate.

RESULTS ON ANIMAL SUBSTANCES.

The data in Table 1 show that, as tested by the recovery of added phosphates, the magnesia mixture method gives results apparently characterized by a high degree of accuracy. The recovery of added phosphates was 96 per cent with liver, 97 per cent with flesh, 99 per cent with brain and 100 per cent with blood.

In consideration of the close agreement of triplicates, the high percentage of recovery of added phosphates, and the amounts of coagulum from which the phosphates were recovered, these results are considered a satisfactory demonstration of the reliability of the method.

In the further scrutiny and analysis of the method, however, it was deemed advisable to test individually certain of its details. Blood was selected for this work, since the ready decomposition of its phosphocarnic acid was considered likely to reveal improper procedure. The results of these studies on blood are set forth in Tables 2 to 5. Table 2 gives results from a study of the effects of heat and ammonium sulphate in this estimation on a cold water extract of steer blood. This extract was obtained through the use of a centrifuge.

TABLE 1.

Test of magnesia mixture method for inorganic phosphorus in animal tissues by recovery of added phosphates (Analyses by F. M. Beegle).

[A = Without phosphates; B = With added phosphates.]

SAMPLE AND DETERMINATION	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE[1]	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	ADDED PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
	grams	*grams*	*per cent*	*grams*	*grams*	*per cent*
Blood:						
A-1	31.30	0.0069	0.00614	...	...	...
A-2	30.00	0.0069	0.00641	...	...	...
A-3	25.00	0.0051	0.00568	...	...	...
Average	...	...	0.00607	...	...	...
B-1	26.10	0.0558	...	...	0.0501	...
B-2	28.20	0.0563	...	...	0.0501	...
B-3	30.50	0.0572	...	...	0.0505	...
Average	...	...	...	0.0497	0.0502	101.00
A-1	33.70	0.0064	0.00529	...	...	...
A-2	33.60	0.0060	0.00505	...	...	...
A-3	31.20	0.0060	0.00544	...	...	...
Average	...	...	0.00526	...	...	...
B-1	30.40	0.0550	...	...	0.0493	...
B-2	32.20	0.0557	...	...	0.0496	...
B-3	35.80	0.0568	...	...	0.0500	...
Average	...	...	...	0.0496	0.0496	100.00
Brain:						
A-1	8.5600	Lost	...	...	...	...
A-2	7.7011	0.0176	0.0636	...	...	...
A-3	9.2368	0.0209	0.0630	...	...	...
Average	...	...	0.0633	...	...	...
B-1	10.7215	0.0507	...	...	0.0263	...
B-2	9.2277	0.0474	...	...	0.0264	...
B-3	10.5182	0.0502	...	...	0.0263	...
Average	...	...	...	0.0266	0.0263	98.87
Flesh:						
A-1	13.4653	0.0272	0.0562	...	...	...
A-2	10.3444	0.0207	0.0557	...	...	...
A-3	11.1769	0.0223	0.0555	...	...	...
Average	...	...	0.0558	...	...	...
B-1	10.9638	0.0694	...	...	0.0474	...
B-2	11.7942	0.0725	...	...	0.0488	...
B-3	11.3154	0.0708	...	...	0.0481	...
Average	...	...	...	0.0496	0.0481	96.97
Liver:						
A-1	16.2155	0.0627	0.1077	...	...	...
A-2	13.8000	0.0552	0.1144	...	...	...
A-3	14.4309	0.0519	0.1002	...	...	...
Average	...	...	0.1064	...	...	...
B-1	14.9094	0.1045	...	...	0.0475	...
B-2	14.9658	0.1054	...	...	0.0482	...
B-3	16.2232	0.1094	...	...	0.0474	...
Average	...	...	...	0.0496	0.0477	96.16

[1] All blanks deducted.

In sets A and C the phosphates were precipitated direct, with magnesia mixture, with and without ammonium sulphate added (in the cold) before precipitation. The results were practically identical, and show that, in the cold, ammonium sulphate does not affect inorganic phosphate determination in blood. Sets B and D were boiled with different amounts of ammonium sulphate added.

TABLE 2.

Effects of boiling and varying amounts of ammonium sulphate in the estimation of inorganic phosphorus in steer blood by the magnesia mixture method. (Analyses by F. M. Beegle).

[Cold water extracts.]

TREATMENT[1]	SAMPLE NO.	VOLUME OF EXTRACT	WEIGHT OF MAGNESIUM PYROPHOSPHATE	WEIGHT OF PHOSPHORUS
		cc.	gram	mg.
Extract precipitated direct with magnesia mixture	A-1........	300	0.0091	2.535
	A-2........	300	0.0087	2.424
	A-3........	300	0.0087	2.424
	Average...	....	....	2 461
Extract brought to boiling; ammonium sulphate added to make 1.25 per cent solution, then boiled for 10 minutes	B-1........	300	0.0079	2.201
	B-2........	300	0.0078	2.173
	B-3........	300	0 0081	2.257
	Average....	....	....	2.210
Same as A, with ammonium sulphate added before precipitation to make 1.25 per cent solution	C-1........	300	0.0085	2.368
	C-2........	300	0.0085	2.368
	C-3........	300	0.0086	2.396
	Average...	....	....	2.374
Same as B, with ammonium sulphate added to make 3⅓ per cent solution	D-1........	300	0.0075	2.090
	D-2........	300	0.0074	2.062
	D-3........	300	0.0073	2.034
	Average...	....	....	2.062

[1] All of the extracts and filtrates were precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then, after standing a short period, 25 cc. of ammonia (specific gracity, 0.90).

The boiling and precipitation of inorganic phosphates in a 1.25 per cent solution of ammonium sulphate (20 cc. of 20 per cent ammonium sulphate as specified) gave weights of magnesium pyrophosphate 0.15 mg. greater than those obtained from boiling and precipitation in a 3.33 per cent solution of ammonium sulphate. The results were, in both B and D, appreciably lower than those obtained from A and C, with and without ammonium sulphate, but without boiling. These results show, therefore, that ammonium sulphate, in the cold, is without influence on

TABLE 3.

Completeness of extraction and effects of boiling and ammonium sulphate in the estimation of inorganic phosphorus in calf blood by the magnesia mixture method (Analyses by F. M. Beegle).

[Cold water extracts.]

TREATMENT[1]	SAMPLE NO.	VOLUME OF EXTRACT	WEIGHT OF MAGNESIUM PYROPHOSPHATE	WEIGHT OF MAGNESIUM PYROPHOSPHATE ADDED	ADDED PHOSPHORUS RECOVERED	
		cc.	*grams*	*gram*	*gram*	*per cent*
Extract precipitated direct with magnesia mixture	A-1	300	0.0107			
	A-2	300	0.0105			
	A-3	300	0.0103			
	Average		0.0105			
Same as A-1, A-2, A-3 plus 25 cc. of phosphate solution	A-4	300	0.0619			
	A-5	300	0.0618			
	A-6	300	0.0620			
	Average		0.0619	0.0517	0.0514	99.42
Extract brought to boiling, 20 cc. of 20 per cent ammonium sulphate added, and boiled for 10 minutes, filtered, and washed by decantation	B-1	300	0.0083			
	B-2	300	0.0086			
	B-3	300	0.0091			
	Average		0.0087			
Same as B-1, B-2, B-3 but coagulum ground with fine sand for more complete extraction and washing	B-4	300	0.0090			
	B-5	300	0.0084			
	B-6	300	0.0088			
	Average		0.0087			
Same as B-1, B-2, B-3 plus 25 cc. of phosphate solution	C-1	300	0.0603			
	C-2	300	0.0601			
	C-3	300	0.0604			
	Average		0.0603	0.0517	0.0516	99.86
Same as B-4, B-5, B-6 plus 25 cc. of phosphate solution	C-4	300	0.0601			
	C-5	300	0.0609			
	C-6	300	0.0602			
	Average		0.0604	0.0517	0.0517	100.00

[1] All of the extracts and filtrates were precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then, after standing a short period, 25 cc. of ammonia (specific gravity, 0.90).

the inorganic phosphorus estimation, but that boiling and ammonium sulphate together not only do not split off inorganic from organic phosphorus compounds, but, as shown by the lower results obtained, cause a coagulation and precipitation of organic phosphorus in the water extract which, when not so precipitated, remains in solution until precipitated by the magnesia mixture, after which it may be hydrolyzed by nitric acid in the later steps of the phosphorus estimation.

Considering the possibility that the lower results obtained in the presence of ammonium sulphate might be due to the mechanical inclusion of phosphates in the coagulum, another set of determinations was made, as reported in Table 3. The grinding of the coagulum with sand, to allow more complete extraction and washing, gave exactly the same result as did the washing of the coagulum by decantation, in the usual way. Therefore, the extraction, as usually carried out, is complete, and coagulation by boiling and ammonium sulphate does not lock up inorganic phosphate by mechanical inclusion. Further, as in the previous set of analyses, lower results were obtained with boiling and ammonium sulphate than

TABLE 4.

Effects of boiling and ammonium sulphate in the estimation of inorganic phosphorus in steer blood by the magnesia mixture method (Analyses by F. M. Beegle).

[Cold water extracts.]

TREATMENT[1]	SAMPLE NO.	VOLUME OF EXTRACT	WEIGHT OF MAGNESIUM PYROPHOSPHATE ADDED	WEIGHT OF PHOSPHORUS
		cc.	*gram*	*mg.*
Extract precipitated direct with magnesia mixture	A-1........	200	0.0075	2.089
	A-2........	200	0.0070	1.950
	A-3........	200	0.0070	1.950
	Average....	....	0.0072	1.996
Extract precipitated as A-1 A-2, A-3 and precipitate dissolved in acid alcohol (0.2 per cent nitric acid) and phosphorus determined in aliquot of this solution	A-4........	200	0.0076	2.117
	A-5........	200	0.0073	2.031
	A-6........	200	0.0065	1.811
	Average....	....	0.0071	1.987
Extract boiled for 10 minutes with 20 cc. of 20 per cent ammonium sulphate, filtered and precipitated direct	B-1........	200	0.0062	1.727
	B-2........	200	0.0058	1.616
	B-3........	200	[2]0.0096	....
	Average....	....	0.0060	1.671

[1] All of the extracts and filtrates were precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then, after standing a short period, 25 cc. of ammonia (specific gravity, 0.90).

[2] Precipitate of magnesium pyrophosphate fused, not included in average.

with direct precipitation in the cold, though the recovery of added phosphates was perfect in both cases. This reinforces our previous observation as to the precipitation of organic phosphorus from cold-water extracts of blood, along with the inorganic phosphates. Thus, boiling and ammonium sulphate are needed to coagulate a certain water-soluble organic phosphorus fraction of blood in the estimation of inorganic phosphorus by the magnesia mixture method.

The results in Table 4, show that acid alcohol (0.2 per cent nitric acid) will dissolve the organic phosphorus compound which is precipitated, along with the phosphates, by magnesia mixture alone, in cold-water extracts of blood, a separation of the organic from the inorganic phosphorus in this precipitate, by the use of this reagent, therefore, not being possible.

In Table 5 are results from tests made to determine (1) whether hot water or ammonium sulphate should be used in the completion of the extraction of the coagulum from the boiling with ammonium sulphate, and (2) whether, in the extraction of blood, the partial extracts should be filtered through sand on linen or through filter paper.

Lower results (and, therefore, in the light of the previous evidence, more nearly accurate results) were obtained when a 3.33 per cent solution of ammonium sulphate, rather than hot water, was used in the completion of the extraction of the coagulum. The recovery of added phosphates was also higher when the ammonium sulphate solution was used to complete the extraction of the coagulum. Filtration of the blood extracts through paper was found preferable to filtration through sand on linen.

This table reports a further test of the desirability of using ammonium sulphate in the completion of the extraction of the coagulum from the preliminary boiling with ammonium sulphate. As in the previous work the results obtained favored the use of 3.33 per cent ammonium sulphate solution to complete the extraction since this procedure led to lower results for inorganic phosphorus and more nearly perfect recovery of added phosphates.

There are also given results from a comparison of the use of different amounts of ammonium sulphate in the coagulation and extraction of blood. No advantage could be demonstrated as due to the use of solutions of ammonium sulphate more concentrated than the 3.33 per cent solution used in the preceding tests; that is, the use of a 3.33 per cent solution gave lower, and apparently more nearly accurate results than were obtained with a 1.25 per cent solution, while further increase of the concentration of the ammonium sulphate solution did not lead to further decrease in inorganic phosphate.

TABLE 5.

Use of ammonium sulphate and filtration in the estimation of inorganic phosphorus in steer blood by the magnesia mixture method (Analyses by F. M. Beegle).

[Hot water ammonium sulphate extracts.]

TREATMENT[1]	SAMPLE NO.	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE[2]	MAGNESIUM PYROPHOSPHATE ADDED	ADDED PHOSPHORUS RECOVERED	
		grams	*gram*	*gram*	*gram*	*per cent*
Sample extracted in usual way with 20 cc. of 20 per cent ammonium sulphate; filtered through sand on linen	1..........	34.2	0.0079	....	....	....
	2..........	26.6	0.0061	....	....	....
	3..........	30.7	0.0064	....	....	....
	Average....	30.5	0.0068	....	....	....
		1.0	0.000223	....	....	....
Same as 1, 2, 3, plus 25 cc. of phosphate solution	4..........	30.7	0.0583	0.0537	0.0515	....
	5..........	33.1	0.0582	0.0537	0.0508	....
	6..........	38.2	0.0590	0.0537	0.0505	....
	Average....	....	....	....	0.0509	94.78
Sample extracted as usual; subsequent extractions made with $3\frac{1}{3}$ per cent hot ammonium sulphate; filtered through sand on linen	7..........	28.4	0.0040	....	....	....
	8..........	34.2	0.0060	....	....	....
	9..........	39.1	0.0069	....	....	....
	Average....	33.9	0.0056	....	....	....
		1.0	0.000165			
Same as 7, 8, 9, plus 25 cc. of phosphate solution	10.........	37.6	0.0590	0.0537	0.0528	....
	11.........	40.9	0.0590	0.0537	0.0522	....
	12.........	32.4	0.0576	0.0537	0.0522	....
	Average....	....	....	....	0.0524	97.57
Sample extracted usual way, plus 25 cc. of phosphate solution; filtered through paper instead of sand on linen (4, 5, 6)	13.........	32.6	0.0583	0.0537	0.0510	....
	14.........	33.9	0.0596	0.0537	0.0520	....
	Average....	....	....	....	0.0515	95.90
Sample extracted usual way plus 25 cc. of phosphate solution; subsequent extraction with $3\frac{1}{3}$ per cent ammonium sulphate; filtration through paper instead of sand on linen (10, 11, 12)	15.........	31.5	0.0600	0.0537	0.0548	....
	16.........	37.4	0.0603	0.0537	0.0541	....
	Average....	....	....	....	0.0544	101.303

[1] All filtrates were precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then, after standing a short period, 25 cc. of ammonia (specific gravity 0.90).

[2] All blanks deducted.

TABLE 5—Continued.

TREATMENT[1]	SAMPLE NO.	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE[2]	MAGNESIUM PYROPHOSPHATE ADDED	ADDED PHOSPHORUS RECOVERED	
		grams	*gram*	*gram*	*gram*	*per cent*
Sample extracted with 20 cc. of 20 per cent ammonium sulphate as usual; all subsequent extractions made with hot water	A-1	32.0	0.0078	....	....	....
	A-2	32.8	0.0080	....	....	....
	A-3	34.6	0.0083	....	....	....
	Average	33.1	0.0080			
		1.0	0.00024	....	....	....
Same as A-1, A-2, A-3 plus 25 cc. of phosphate solution	A-4	33.5	0.0573	....	....	....
	A-5	34.1	0.0569	....	....	....
	A-6	26.3	0.0556	....	....	....
	Average	31.3	0.0566	0.0496	0.0491	98.99
Same as A-1, A-2, A-3 except all subsequent extractions made with $3\frac{1}{3}$ per cent ammonium sulphate solution instead of water	B-1	33.7	0.0064	....	....	....
	B-2	33.6	0.0060	....	....	....
	B-3	31.2	0.0060	....	....	....
	Average	32.8	0.0061	....	....	....
		1.0	0.00019			
Same as B-1, B-2, B-3, plus 25 cc. of phosphate solution	B-4	30.4	0.0550	....	....	....
	B-5	32.2	0.0556	....	....	....
	B-6	35.8	0.0568	....	....	....
	Average	32.8	0.0558	0.0496	0.0497	100.20
	Blank 1	....	0.0005	....	....	....
	Blank 2	....	0.0005	....	....	....
	Blank 3	....	0.0004	....	....	....

[1] All of the above filtrates precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then after standing a short period, 25 cc. of ammonia (specific gravity, 0.96).
[2] All blanks deducted.

TABLE 5—*Concluded.*

TREATMENT[1]	SAMPLE NO.	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE[2]	MAGNESIUM PYROPHOSPHATE ADDED	ADDED PHOSPHORUS RECOVERED	
		grams	*gram*	*gram*	*gram*	*per cent*
Sample extracted with 3 per cent ammonium sulphate solution throughout	A-1	31.3	0.0069	....	....	....
	A-2	30.0	0.0069	....	....	....
	A-3	25.0	0.0051	....	....	....
	Average	28.76	0.0063	....	....	....
		1.0	0.00022			
Same as A-1, A-2, A-3, plus 25 cc. of phosphate solution	A-4	26.1	0.0558	....	....	....
	A-5	28.2	0.0563	....	....	....
	A-6	30.5	0.0572	....	....	....
	Average	28.3	0.0564	0.0497	0.0502	101.00
Sample extracted with 4 per cent ammonium sulphate solution throughout	B-1	27.8	0.0071	....	....	....
	B-2	27.0	0.0069	....	....	....
	B-3	30.8	0.0074	....	....	....
	Average	28.5	0.0071	....	....	....
		1.0	0.00025			
Same as B-1, B-2, B-3 plus 25 cc. phosphate solution	B-4	31.4	0.0584	....	....	....
	B-5	31.2	0.0579	....	....	....
	B-6	41.3	0.0576	....	....	....
	Average	34.6	0.0580	0.0497	0.0493	99.20
Sample extracted with 5 per cent ammonium sulphate solution throughout	C-1	28.1	0.0065	....	....	....
	C-2	28.2	0.0070	....	....	....
	C-3	30.5	0.0067	....	....	....
	Average	28.9	0.0067			
		1.0	0.00023	....	....	....
Same as C-1, C-2, C-3, plus 25 cc. of phosphate solution	C-4	30.5	0.0582	....	....	....
	C-5	26.9	0.0575	....	....	....
	C-6	45.5	0.0589	....	....	....
	Average	34.3	0.0582	0.0497	0.0503	101.21
500 cc. of 5 per cent ammonium sulphate plus 25 cc. of phosphate solution	....	....	0.0498	....	....	....
	....	....	0.0496	....	....	....
	....	....	0.0497	0.0497	....	100.00

[1]All of the above filtrates precipitated by adding 50 cc. of magnesia mixture to the cool solution, and then after standing a short period, 25 cc. of ammonia (specific gravity, 0.90).
[2]All blanks deducted.

CONCLUSIONS ON INORGANIC PHOSPHORUS ESTIMATION IN ANIMAL SUBSTANCES.

(1) The magnesia mixture method gives satisfactorily agreeing results on blood, brain, liver and flesh, with a recovery of 96 to 100 per cent of added phosphates.

(2) Neither ammonium sulphate, nor boiling and ammonium sulphate together, as used in the magnesia mixture method, were found to cause a splitting off of inorganic from organic phosphorus in blood.

(3) The use of heat and ammonium sulphate, as in the magnesia mixture method, gives lower results than are obtained without heat and ammonium sulphate, though the recovery of added phosphates is perfect; and evidence was obtained that these lower results were due not to inclusion of phosphates in the coagulum obtained by the use of heat and ammonium sulphate, but to the precipitation of water-soluble organic phosphorus which, without the use of heat and ammonium sulphate, yields up its phosphorus as inorganic phosphate, under the influence of the nitric acid used in the subsequent steps of the inorganic phosphorus estimation.

(4) It was found advisable to wash the coagulum with 3.33 per cent ammonium sulphate rather than with hot water. A more concentrated solution was shown not to be necessary.

(5) In the case of blood, the filtration of the extract through paper was found preferable to the filtration through sand on linen, which is necessary in the case of brain.

INORGANIC PHOSPHORUS ESTIMATION IN VEGETABLE SUBSTANCES.

In accordance with the recommendation of the association, the referee work on inorganic phosphorus in vegetable substances for the year 1914 covered the following points in a study of the acid-alcohol method of Forbes, Lehmann, Collison and Whittier:[1] (a) The completeness of extraction; (b) the effect of using much larger amounts of magnesia mixture in the precipitation; (c) the allowing of more time for the precipitation with magnesia mixture; (d) the facilitating of the filtration by the use of the centrifuge; and (e) the use of mechanical means to break up the precipitate in acid alcohol to insure the complete solution of the phosphate.

RESULTS ON VEGETABLE SUBSTANCES.

The following tabular data set forth the results of this study, the general method being that of the recovery of known amounts of phosphates introduced into the estimation. Throughout this work the centrifuge was used to facilitate filtration of the 0.2 per cent hydrochloric acid extracts. The advantage derived from this treatment was very great. Extracts

[1] Ohio Agr. Exper. Sta. Bul. 215; This Journal, 1915, **1**: 235.

which it was impossible otherwise to filter within a reasonable time were, with the aid of the centrifuge, filtered without difficulty or delay.

Other constant conditions in this work were the use of an extreme amount, 50 cc., of magnesia mixture in the preliminary precipitation (instead of 10 cc. as usual), and 3 days' time were allowed in all cases for the completion of this precipitation.

Table 6 reports results from a test of the acid-alcohol method of Forbes and associates, with alfalfa hay, by the method of recovery of added phosphates, and a test of the completeness of extraction. Alfalfa was selected for this test as that substance which, in our previous experience, had given us the most trouble, and the poorest results. Samples 4, 5, and 6 as compared with 1, 2, and 3, show that the recovery of added phosphates was incomplete, except in the case of Sample 5, in which case, as explained in the footnote below the table, on account of the accidental breaking of the first filter paper, the precipitation was finally made in the presence of the pulp from this paper. In this case the recovery was complete. This accidental result sustained our hypothesis that our difficulty in recovering added phosphates was due to the physical character of the first magnesia mixture precipitate, its gummy character rendering impossible the complete separation, in acid-alcohol, of the inorganic phosphates from the phytin and other substances present. This point was given further study.

Determinations 7a, 8a, and 9a were made in the same way as 1, 2, and 3. Determinations 7b, 8b, and 9b were second extractions of the residues from determinations 7a, 8a, and 9a. The results from the second extraction equalled only the residual amount of phosphate clinging to the sample, from the first extraction; that is, no more inorganic phosphate was dissolved in a 3-hour extraction, following the 3-hour extraction regularly followed in the method. The extraction was complete at the end of the first 3-hour treatment.

Considering the second set of samples in the table, with Samples 1 to 9 the first magnesia mixture precipitates were extracted with 200 cc. of 0.2 per cent nitric acid in alcohol instead of 100 cc., as usual, in order to test the sufficiency of the latter amount to neutralize the ammonia remaining in the precipitates, and to dissolve the phosphates. With Samples 10 to 12 the usual 100 cc. of acid alcohol were used. The comparison shows that 100 cc. of acid were probably sufficient, though the result from Sample 11, for some unknown reason, was low.

The second and third sets of triplicates, Samples 4 to 9, contrast results from the addition of phosphates to be recovered after the extraction (immediately before precipitation), and previous to the 3-hour extraction. We see here no evidence of a retention of added phosphates by the solid substance of the sample.

Determinations 13 to 15 were made to ascertain whether or not a complete recovery of phosphates could be obtained from filter paper pulp. It was possible to recover the phosphates completely. This test has a bearing on work to follow, and shows that the incomplete recovery of added phosphates could not be due to the presence of filter paper pulp.

The recovery of added phosphates in these estimations on alfalfa was fairly satisfactory.

TABLE 6.

Inorganic phosphorus estimation on alfalfa hay by the acid alcohol method.

[Weight of samples, 10 grams; results represent one-half of this amount.]

TREATMENT	SAMPLE NO.	WEIGHT OF MAGNESIUM PYROPHOSPHATE	PHOSPHORUS	ADDED MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
		gram	*per cent*	*gram*	*gram*	*per cent*
Without added phosphate	1	0.0176	....	....	....	....
	2	0.0181	....	....	....	....
	3	0.0178	....	....	....	....
	Average	0.0178	0.0992	....	....	....
With added phosphate	4	0.0425	....	0.0299	0.0246	82.27
	[1]5	0.0477	....	0.0299	0.0299	100.00
	6	0.0404	....	0.0299	0.0226	75.58
	Average	....	....	....	....	85.95
Without added phosphate; same as 1, 2, and 3	7a	0.0182	....	....	....	....
	8a	0.0181	....	....	....	....
	9a	0.0181	....	....	....	....
	Average	0.0181	0.1008	....	....	....
Second extraction of samples 7a, 8a and 9a	7b	0.0062	....	[2]0.0060	....	....
	[3]8b	0.0060	....	0.0060	....	....
	9b	0.0058	....	0.0060	....	....
	Average	....	....	....	....	....
Filtrate precipitated with 50 cc. of magnesia mixture plus 20 cc. of ammonium hydroxid; 20 cc. of acid alcohol used to extract magnesia mixture precipitate	1	0.0183	....	....	....	....
	2	0.0180	....	....	....	....
	3	0.0184	....	....	....	....
	Average	0.0182	....	....	....	....

[1] During the filtration of the first magnesia mixture precipitate the filter paper broke. This paper was then added to the beaker containing the precipitate, beaten up into a pulp, and the filtration continued through a new paper.

[2] Magnesium pyrophosphate equivalent to phosphorus in solution, from previous extraction, remaining in the sample.

[3] Samples 7b, 8b, and 9b are the extraction residues from 7a, 8a, and 9a, with filter paper added, and also enough 0.2 per cent hydrochloric acid solution to make the original volume of 300 cc. This set was extracted for 3 hours to test the completeness of the previous extraction.

TABLE 6—*Continued.*

TREATMENT	SAMPLE NO.	WEIGHT OF MAGNESIUM PYROPHOSPHATE	PHOSPHORUS	ADDED MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
		gram	*per cent*	*gram*	*gram*	*per cent*
Same plus 25 cc. of phosphate solution just before precipitation	4	0.0603	....	0.04485	....	....
	5	0.0606	....	....	....	....
	6	0.0604	....	....	....	....
	Average	0.0604	....	....	0.0429	94.1
Same as 1, 2 and 3 of this set except that 25 cc. of phosphate solution were added, shaken for 3 hours, filtered and filtrate precipitated as 1, 2 and 3	7	0.0466	....	0.0299	0.0284	94.98
	8	0.0466	....	0.0299	0.0284	....
	9	0.0472	....	0.0299	0.0290	96.99
	Average	....	....	....	....	95.98
Same as 7, 8 and 9 of this set, except that only 100 cc. of acid alcohol were used in extraction of magnesia mixture precipitate	10	0.0467	....	....	0.0285	95.32
	11	0.0447	....	....	0.0265	88.63
	12	0.0464	....	....	0.0282	94.31
	Average	....	....	....	....	92.75
25 cc. of phosphate solution put in flasks plus 175 cc. of 0.2 per cent nitric acid in alcohol plus 2 filter papers, shaken, filtered and aliquot taken for precipitation	13	0.0404	....	0.03987	0.0404	101.1
	14	0.0404	....	....	0.0404	....
	15	0.0402	....	....	0.0402	....
	Average	....	....	....	....	....

Table 7 sets forth results of estimations on blue grass and rice polish, with and without added phosphate, with filter paper pulp added, in the first precipitation, to maintain a readily-permeable condition in the precipitate. With blue grass the results may be considered perfect. With rice polish the recovery of added phosphates was 90 per cent efficient. The loss amounted to 0.0025 gram of magnesium pyrophosphate per determination.

The determinations on rice polish, wheat middlings, and soy beans were with and without added phosphates, with phenol added to the extractive reagent to prevent possible enzym action involving phosphorus compounds, and with filter paper pulp added to facilitate solution of the phosphates in the precipitate. The recovery of added phosphates was unsatisfactory; the effect of the phenol on the physical condition of the first magnesia mixture precipitate being of a nature to hinder the dissolving out of the included phosphates.

The determinations on soy beans, wheat middlings, and oat straw were with and without added phosphate, with filter paper pulp, and without phenol added to the extracting sample. With oat straw the results are satisfactory. With soy beans the recovery of added phosphates was incomplete, while with wheat middlings 3 mg. more phosphate seem to have been recovered than were added. In this case the imperfection of the result can not be ascribed as usual, to the physical condition of the magnesia mixture precipitate. Here, it seems, that there must have been a cleavage, of inorganic from organic phosphorus, either enzymatic or as a result of the extractive treatment.

TABLE 7.

Inorganic phosphorus estimation on vegetable substances by the acid alcohol method (Analyses by F. M. Beegle.)

[Weight of samples, 10 grams; results represent one-half of this amount.]

SUBSTANCE	TREATMENT	SAMPLE NO.	WEIGHT OF MAGNESIUM PYROPHOSPHATE	PHOSPHORUS	ADDED PHOSPHORUS AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
			gram	*per cent*	*gram*	*gram*	*per cent*
Blue grass	Filtrate precipitated with 50 cc. of magnesia mixture plus 25 cc. of ammonium hydroxid plus paper pulp	1	0.0373	0.2078			
		2	0.0371	0.2067			
		3	0.0386	0.2151			
		Average		0.2099			
	Same plus 25 cc. phosphate solution	4	0.0624		0.0250	0.0251	100.04
		5	0.0623		0.0250	0.0252	100.08
		6	0.0633		0.0250	0.0247	98.80
		Average					
Rice polish	Same as 1, 2, and 3	7					
		8	0.0070				
		9	0.0070				
		Average	0.0070	0.0390			
	Same as 1, 2, and 3, plus 25 cc. phosphate solution	10	0.0295		0.0250	0.0225	
		11					
		12	0.0295		0.0250	0.0225	
		Average				0.0225	90.00
	Filtrate precipitated with 50 cc. of magnesia mixture plus 25 cc. of ammonium hydroxid	1					
		2	0.0080	0.0446			
		3	0.0072	0.0401			
		Average		0.0424			
Rice polish plus phosphate		4	0.0543		0.0768	0.0467	60.81
		5	0.0461		0.0768	0.0385	50.13
		6	0.0443		0.0768	0.0367	47.79
		Average					52.91
Middlings		7	0.0132				
		8	0.0133				
		9	0.0129				
		Average	0.0131	0.0724			

TABLE 7—*Continued.*

SUBSTANCE	TREATMENT	SAMPLE NO.	WEIGHT OF MAGNESIUM PYROPHOSPHATE	PHOSPHORUS	ADDED PHOSPHORUS AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
			gram	per cent	gram	gram	per cent
Middlings plus phosphate.......	....	10	0.0830	....	0.0768	0.0699	91.01
		11	0.0864	....	0.0768	0.0733	95.44
		12	0.0847	....	0.0768	0.0716	93.23
		Average	....	....	....	....	93.23
Soy beans..........	....	13	0.0102	....	....	....	....
		14	0.0105	....	....	....	....
		15	0.0102	....	....	....	....
		Average	0.0103	0.0574	....	....	....
Soy beans plus phosphate.......	....	16	0.0790	....	0.0768	0 0687	89.45
		17	0.0801	....	0.0768	0.0698	90.89
		18	0.0823	....	0.0768	0.0720	93.75
		Average	0.0805	....	....	....	91.36
Soy beans..........	Usual method, plus filter paper pulp; without phosphate	1	0.0102	....	....	....	....
		2	0.0103	....	....	....	....
		3	0.0101	....	....	....	....
		Average	0.0102	0.0568	....	....	....
Soy beans plus phosphate.......	Usual method, plus filter paper pulp; with phosphate	4	0.0336	....	0.0261	0.0234	90.03
		5	0.0345	....	0.0261	0.0243	93.10
		6	0.0347	....	0.0261	0.0245	93.87
		Average	....	....	....	....	92.33
Middlings..........	Same as 1, 2, and 3 of this set	7	0.0135	....	....	....	....
		8	0.0131	....	....	....	....
		9	0.0139	0.0752	....	....	....
		Average	0.0135	....	....	....	....
Middlings plus phosphate.......	Same as 4, 5, and 6 of this set	10	0.0432	....	0.0261	0.0297	113.79
		11	0.0430	....	0.0261	0.0295	113.02
		12	0 0418	....	0.0261	0.0283	108.42
		Average	....	....	....	....	111.74
Oat straw..........	Same as 1, 2, and 3 of this set	13	0.0062	....	....	....	....
		14	0.0058	....	....	....	....
		15	0.0061	....	....	....	....
		Average	0.0060	0.0334	....	....	....
Oat straw plus phosphate.......	Same as 4, 5, and 6 of this set	16	0.0312	....	0.0261	0.0252	96.55
		17	0.0319	....	0.0261	0.0259	99.23
		18	0.0318	....	0.0261	0.0258	98.85
		Average	....	....	....	....	98.21

CONCLUSIONS ON INORGANIC PHOSPHORUS ESTIMATION IN VEGETABLE SUBSTANCES.

(1) The use of the centrifuge very greatly facilitates the filtration of dilute aqueous acid extracts of vegetable substances.

(2) The introduction of filter paper pulp into such an extraction materially assists in the maintenance of an easily-penetrable condition in the magnesia mixture precipitate.

(3) It was found possible to recover phosphates completely from filter paper pulp alone as used in this work.

(4) Evidence was obtained sustaining previous conclusions that a 3-hour extraction in 0.2 per cent hydrochloric acid is sufficient for the extraction of inorganic phosphates from finely-ground samples of vegetable substances.

(5) Modification of the acid alcohol method of Forbes and associates by the introduction of filter paper pulp into the extraction, the use of excessive amounts of magnesia mixture in the first precipitation, and allowing unusual duration of time for precipitation gave apparently perfect results, as judged by recovery of added phosphates, in certain cases, but unsatisfactory results in others.

(6) Incompleteness of recovery of added phosphates was shown to be due not to retention of phosphates by the solid substance of the sample, but, in most cases to the difficulty of dissolving the phosphates out of the bulky and often gummy precipitate obtained from the extract by the use of magnesia mixture and ammonia.

(7) We are unable, therefore, to recommend this method, or any other, as reliable for the estimation of inorganic phosphorus in vegetable substances generally.

REPORT ON HEAVY METALS IN FOODS.

By E. L. P. Treuthardt (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The work this year consisted in the study of the methods recommended in 1913 for determining arsenic and tin, and followed closely the lines worked upon last year. After communicating with R. E. Remington, associate referee on baking powders, it was decided that the subject of the determination of lead in baking powder and baking chemicals should be included in his work, and consequently it was not included in the work on heavy metals.

ARSENIC.

SAMPLES.

Two samples were made up for testing the methods. One was a sugar sirup containing 7.4 mg. of arsenic trioxid per kilo, and the other was a sweetened condensed milk containing 3.0 mg. of arsenic trioxid per kilo.

METHODS.

The methods tested were modifications of the Gutzeit method, mainly adapted from Bureau of Chemistry Circular 102. The procedures differed from those used in 1913 chiefly in the following details: (1) The acid digestion was conducted in porcelain dishes instead of in flasks;

(2) the sulphuric acid in the generator bottles for making determinations and standards was 1 to 8 strength instead of 1 to 4; (3) the reduction to arsenite was made on the aliquot portions instead of on the entire sample; (4) the standards were reduced before adding zinc.

Method 1. Destruction of organic matter by digestion.—Weigh 25 grams of sample into a porcelain casserole, cover the casserole and add 10 cc. of arsenic-free nitric acid. Heat until vigorous action is over, cool and add 10 cc. of arsenic-free sulphuric acid. Heat on a wire gauze over a flame until the mixture turns dark brown or black, then add more nitric acid in 10 cc. portions, heating between each addition until the liquid remains colorless or yellow, even after the evolution of SO_3 fumes. To remove completely all nitric or nitrous acids, evaporate to about 5 cc., and if on addition of water to the cooled acid, nitrogen peroxid fumes are evolved, a second evaporation to white fumes is necessary. Dilute the acid solution, transfer to a 100 cc. flask and rinse out the casserole with water; cool and make up to 100 cc. with water. Introduce 20 cc. of this solution into a 2 ounce generator bottle, add 20 cc. of 1 to 4 sulphuric acid and 0.75 gram of potassium iodid. Heat to about 90°C., add 3 drops of stannous chlorid solution and continue heating for 10 minutes. Cool the bottles in a pan containing water and ice. When cold add about 15 grams of stick zinc in several pieces and connect with the tubes as on page 2 of Circular 102. Keep the bottles in ice water for 15 minutes; then take out and allow to run for 1 hour longer. Run a blank test with reagents alone.

Method 2.—Repeat the above procedure, omitting the use of potassium iodid. Instead of the iodid, use about 8 drops of 40 per cent stannous chlorid solution.

Method 3. Separation from organic matter by precipitation with magnesium phosphate mixture.—*Sample 1:* Weigh out 25 grams and heat with bromin water in slight excess. Neutralize with ammonia, add 2 grams of arsenic-free disodium hydrogen phosphate and precipitate with an excess of magnesia mixture. Add a slight excess ammonia so that its concentration is about 2.5 per cent. Instead of the phosphate, a corresponding amount of phosphoric acid solution may be used and the solution neutralized with ammonia. Filter and wash the precipitate with 2.5 per cent ammonia. Drain and dissolve the precipitate with 1 to 4 sulphuric acid, and wash the filter thoroughly with the same. Make up to 100 cc. with the 1 to 4 acid. Take 20 cc. portions of this solution, add 20 cc. of water and 0.75 gram of potassium iodid, and proceed with the reduction as in Method 1. Note that by adding water to the acid solution, about the same acid strength is attained (1:8), as by adding acid to the aqueous solution in Method 1.

Sample 2: Weigh out 25 grams, add 50 cc. of water and 25 cc. of arsenic-free nitric acid and boil until the solution is clear. A slight amount of fat on the surface may be disregarded. Neutralize with ammonia, add the phosphate and magnesia mixture and proceed as with Sample 1.

Method 4.—Any other modification of the Gutzeit method that has been found satisfactory.

STANDARDS.

Make up standards as on page 2 of Circular 102. The generator bottle should have 40 cc. solution of 1 to 8 sulphuric acid strength. Add several drops of stannous chlorid solution to the standards and heat for 10 minutes. Cool, add 15 grams of stick zinc, and run the same as the samples, having the bottles in ice water 15 minutes at the start.

REAGENTS.

All reagents should be arsenic-free by test or else the arsenic content should be corrected for by blanks. Potassium iodid is used in a 15 or 20 per cent solution. Stannous chlorid is made 40 per cent in concentrated hydrochloric acid.

RESULTS.

Reports as received from seven collaborators are tabulated. H. Runkel used mercuric chlorid instead of bromid paper in making the tests. In Sample 2 by Method 3 he digested on a steam bath for 3 hours with nitric acid instead of boiling.

Coöperative results on arsenic in foods.

[Reported in mg. of arsenic trioxid (As_2O_3) per kilo.]

ANALYST	SAMPLE 1			SAMPLE 2		
	Method			Method		
	1 Digestion	2 Without potassium iodid	3 Precipitation	1 Digestion	2 Without potassium iodid	3 Precipitation
E. H. Berry	6.0, 6.0	5.6, 5.6	6.0, 6.0	1.8, 2.0	2.0, 2.4	2.0, 2.0
C. L. Black	7.5, 7.6	6.2, 6.3	7.8, 7.8	2.6, 2.8	2.2, 2.1	2.6, 2.7
L. D. Elliott	5.2, 4.4	6.0, 6.6, 5.2	5.6, 5.8, 5.4	2.6, 2.6, 1.9	2.8, 2.6, 2.2	1.0, 0.8
E. R. Lyman	6.0, 6.0	6.0	8.0, 7.0	1.6, 2.0	1.6, 1.4	.....
T. F. Pappe	7.4, 6.6	7.4, 7.8	3.4, 3.0, 4.1, 4.6	1.6, 1.6	1.4, 1.4	0.9, 1.1, 0.9, 1.1
H. Runkel	8.4, 8.8	7.2, 7.6	8.2, 7.8	3.4, 3.4	......	....
E. L. P. Treuthardt	5.2, 5.6, 5.6	5.2, 3.8, 8.0, 5.6	2.8, 3.8, 4.0, 4.2	1.8, 1.8, 2.2, 1.8	2.4, 1.8, 1.8, 1.6	1.8, 2.2, 2.6, 1.8
Maximum	8.8	8.0	8.2	3.4	2.8	2.7
Minimum	4.4	3.8	2.8	1.6	1.4	0.8
Average	6.4	6.3	5.5	2.2	1.9	1.7

OTHER MODIFICATIONS TRIED BY COLLABORATORS.

L. D. Elliott: On Sample 1. (*a*) Followed Method 3, but dissolved the magnesium phosphate precipitate in 1 to 3 hydrochloric acid, and added 1 to 3 hydrochloric acid to the generator bottle. Obtained 6.4 and 6.0 mg. of arsenic trioxid per kilo.

(*b*) Repeated (*a*) but used 1 to 6 hydrochloric acid. Obtained 6.0 mg. of arsenic trioxid per kilo.

On Sample 2. (*c*) Followed Method 3 but used 1 to 3 hydrochloric acid as on Sample 1 (*a*). Results obtained with and without using potassium iodid were 0.8 and 0.6 mg. of arsenic trioxid per kilo respectively.

(*d*) Boiled the sample 1 hour with concentrated nitric acid, adding more acid as volume diminished, until solution was complete except for fat. Precipitated with magnesium phosphate and proceeded as in Method 3. Obtained 3.2 mg. of arsenic trioxid per kilo.

(*e*) Digested as in Method 1 but made up to 100 cc. with 1 to 3 hydrochloric acid and added 1 to 3 hydrochloric acid to the generator bottle. Obtained 3.0 mg. of arsenic trioxid per kilo.

H. Runkel: On Sample 1. Followed Method 1 but took an aliquot portion of 5 cc. and used a strip of mercuric chlorid paper 1 mm. in width. Obtained 7.2 and 8.0 mg. of arsenic trioxid per kilo.

E. L. P. Treuthardt: Followed all three methods using 1 to 4 sulphuric acid for making the solutions up to 100 cc. and adding to the generator bottles. Results in mg. of arsenic trioxid per kilo.

SAMPLE 1			SAMPLE 2		
1	2	3	1	2	3
6.0 7.0	6.0 7.4	5.0 6.0	2.4 2.6	2.4 2.6	2.4 2.0

COMMENTS BY COLLABORATORS.

E. H. Berry: There seems to be little choice between the methods. Method 3 has the advantage of eliminating digestion with nitric acid. The use of potassium iodid as a reducing agent in the generator bottle is advantageous in that it makes it easier to obtain uniform stains on the mercuric bromid paper.

C. L. Black: In Method 2 the failure to use potassium iodid appears to decrease the amount of arsin evolved, and the excessive amount of stannous chlorid causes such rapid action even with the generator cooled to 6°C. at the start that the color strip produced is too long and light colored for accurate reading. In Method 3 it was impossible to get off all the arsenic with the strength of acid recommended—the retentive effect of the large amount of salts present necessitates considerably stronger acid.

L. D. Elliott: With the sirup, Method 1 gave consistently low results. Arsin was liberated faster with Method 2 than with Methods 1 or 3. With the condensed milk there was a greater divergence of results obtained by different methods. In this sample the evolution of arsin with Methods 1 and 2 was too slow, and Method 2 does not cause so much difference in speed of evolution or in results as in the sirup. In Method 3 the treatment of condensed milk with dilute nitric acid is inadequate. The fatty residue clogged the filter, rendering filtration slow and tedious and the results were far too low. With the modified method, as given, filtration was more rapid and the results were better.

E. R. Lyman: Prefer the complete oxidation of organic matter. No satisfactory determination was secured on Sample 2 by Method 3. When diluted to 1 to 8 acid strength, there was almost no action on the zinc, while with 1 to 4 acid frothing spoiled the determination.

H. Runkel: All results obtained by Method 2 were low. In one determination by Method 3, which gave a very low result, the magnesium phosphate precipitate had been washed a great deal with 2 per cent ammonia, and the low result was attributed to this cause.

T. F. Pappe: Determinations made on sugar solutions containing known amounts of arsenic showed loss by Method 3. Arsenic trioxid (As_2O_3) was recovered from a sugar solution containing 6 mg. per kilo as follows:

Precipitate	2.8	(Method 3)
Filtrate	2.1	(Method 1)
Washings	0.4	(Method 1)
Total	5.3	

The use of weaker acid and the cooling of the generators cause the stains to be more uniform. The mercuric bromid paper should be marked so that comparison of stains may be made on the same side of the paper. There is a difference in absorbing power of the two surfaces, especially with heavy papers.

E. L. P. Treuthardt: Blank determinations run by Method 1 on 25 gram portions of Sample 2 without any added arsenic gave 0.000 and 0.002 mg. of arsenic trioxid (As_2O_3). This corresponds to an average content of 0.04 mg. of arsenic trioxid (As_2O_3) per kilo. The 1 to 8 acid strength seems to be too dilute and much better results were obtained using 1 to 4 acid. Method 3 recovered less arsenic than Methods 1 and 2.

DISCUSSION.

Comparing the tabulated averages with the actual amounts of arsenic present shows them all to be low. Those for Method 1 are highest and those for Method 3 lowest. The individual results show that most of the individual determinations are low. For Method 1, four results on Sample 1 and two results on Sample 2 which are above the correct value, and on Method 3, five results on Sample 1 which are above the correct value were all obtained from the reports of two of the analysts. Three other results (on Sample 1 by Method 2) are high and two results are correct. With these exceptions, there was always a loss of arsenic, which was proportionally greater on Sample 2. In studying the variations of the individual determinations, the methods show up in the same order as with the averages. The results having a variation of ± 1.4 mg. per kilo (20 per cent) in Sample 1 are:

Method 1, 10 out of 15, or 67 per cent
Method 2, 10 out of 16, or 63 per cent
Method 3, 8 out of 19, or 42 per cent

Those having a variation of ± 0.6 mg. per kilo (20 per cent) in Sample 2 are:

Method 1, 6 out of 17, or 35 per cent
Method 2, 4 out of 15, or 27 per cent
Method 3, 3 out of 14, or 21 per cent

Allowing a greater variation of ± 1.0 mg. per kilo on this sample gives:

Method 1, 9 out of 17, or 53 per cent
Method 2, 8 out of 15, or 53 per cent
Method 3, 4 out of 14, or 29 per cent

Method 1 gives the best results and is considered the most satisfactory. The results are mostly low. This is probably due to the weak strength of acid used. It will be noted from the above work that where the pro-

cedure was modified and a stronger sulphuric or hydrochloric acid was used, higher results were obtained, which came very close to the actual amounts of arsenic in the sample. In future work on the Gutzeit test, it is believed that the general procedure of Method 1 should be followed, that a stronger acid should be used and the relative merits of sulphuric and hydrochloric acids be studied. In this connection, it is well to keep in mind the possibility of the introduction of arsenic through reagents and to the fact that this danger is much greater when hydrochloric acid is used. The use of potassium iodid for reduction seems essential and it is probably advisable to also add it to the standards.

Method 2 was not satisfactory. The low results would probably not be remedied by change of acid strength, as it has been the experience of some of the analysts that not only all of the arsenic is not reduced when stannous chlorid is used alone, but that under the conditions the arsin comes off too rapidly to give satisfactory and consistent stains.

The average results by Method 3 were lower than those obtained by Method 2, but it should be noted that by proper changes in the details of this procedure it is quite probable that it could be made satisfactory. The phosphate precipitation method, as given in Bureau of Chemistry Circular 102, has been developed for comparatively few products and each substance requires a particular procedure. The modification reported by Mr. Elliott seems to be much more satisfactory than the procedure as sent out. While this procedure cannot be of general application, further study of it in connection with specific substances, such as gelatin, sirups, etc., is recommended.

TIN.

SAMPLES.

Two samples were sent to the collaborators. The first consisted of dried meat. To obviate any sampling error, this sample was sent in test tubes, each tube containing the equivalent of about 100 grams of fresh meat, 2 grams of salt and 10 mg. of tin in hydrochloric acid solution. Each portion contained considerable fat. The second sample was an 18 per cent sugar sirup of which 100 gram samples, each containing 30.54 mg. of tin and 40 mg. of ferrous sulphate, were to be taken for analysis.

METHODS.

All samples were first subjected to the following procedure:

DIGESTION OF SAMPLE.

Weigh 100 grams of the finely-ground sample (in Sample 1 take contents of one tube) into an 800 cc. Kjeldahl flask and add 100 to 150 cc. of concentrated nitric acid. Allow to stand overnight or else place the flask on a wire gauze over a free flame and heat until it boils quietly. Add 50 cc. of concentrated sulphuric acid and heat until

white fumes are generated, then add 10 cc. of nitric acid and continue heating as before. Repeat the addition of nitric acid until the solution remains clear after boiling off the nitric acid fumes. The rapidity of digestion depends upon the temperature maintained—the higher the temperature the faster the material is oxidized.

The following methods tried last year were followed this year: 1. Gravimetric method (*This Journal*, 1915, **1**: 257 (*1*)); 2. Volumetric method (Baker) (*This Journal*, 1915, **1**: 258 (*3*)); and 3. Volumetric method (Alexander, Bloomberg, and Lourie) (*This Journal*, 1915, **1**: 259 (*5*)). In the last method after adding the glass beads the procedure may be the same as from that point in the volumetric method (Baker).

RESULTS.

The results obtained from eight collaborators are tabulated. In Method 3, L. D. Elliott used antimony for reduction and the bent tube and bicarbonate solution for cooling. The results are expressed in mg. of tin in the sample taken for analysis (contents of tube in Sample 1 and 100 grams in Sample 2).

Coöperative results on tin in foods.

ANALYST	SAMPLE 1			SAMPLE 2		
	Method			Method		
	1 Gravimetric	2 Baker	3 Alexander, Bloomberg and Lourie	1 Gravimetric	2 Baker	3 Alexander, Bloomberg and Lourie
E. H. Berry	8.7 9.8	10.1 9.9	......	29.9 31.5	23.9 28.3	......
L. D. Elliott	9.3 9.8	......	9.2 9.6 9.6	26.3 22.2	......	22.3 21.5 23.7
W. W. Karnan	10.2 10.4	......	......	30.0 28.8 30.2	......	......
E. R. Lyman	10.9 [1]3.2 [1]3.6	10.5 10.5	......	29.2 29.8 28.1	27.7 30.1 29.1	28.9 28.6
H. M. Miller	......	10.2 10.2	8.4 6.4	......	30.3 30.0	25.4 24.2
H. Runkel	10.5 10.4	7.9 8.6	......	27.0 28.0	25.0 25.7	......
H. R. Smith	10.6 9.5	10.4 9.8	......	27.6 27.2	29.8 27.7	......
E. L. P. Treuthardt	10.8 10.3	10.3	10.9 10.3	[1]18.4 [1]19.7	27.0 23.8	27.8 27.5
Maximum	10.9	10.5	10.9	31.5	30.1	28.9
Minimum	3.2	7.9	6.4	18.4	23.8	21.5
Average	9.2	9.9	9.2	27.1	27.6	25.5
Average excluding determinations marked "1"	10.1	9.9	9.2	28.3	27.6	25.5

[1] So abnormally low that one average was calculated omitting this. This average may be taken as more representative of the method.

Portions of the dried meat used for making Sample 1 of the same size as the samples sent out, but without having tin added, were run as blank tests by two analysts. H. R. Smith found 0.8 mg. of tin using Method 1, and E. L. P. Treuthardt found 0.6, 0.4 and 0.3 mg. of tin using Method 2.

COMMENTS BY COLLABORATORS.

E. H. Berry: Methods 1 and 2 are reasonably accurate, especially after one has used them long enough to learn what the difficulties are. Some erratic results were obtained by the gravimetric method, which were discarded. Those obtained by the volumetric method were all fairly concordant. The latter method is more rapid for a large number of determinations.

L. D. Elliott: Better results were obtained with meat than with sirup with Method 3. A smaller sample of sirup might have been better as the large amount of tin present caused trouble in dissolving the stannic acid precipitate through the filter. In one instance, after titration the filter paper was placed in hydrochloric acid, reduced with antimony and titrated with a result of a 9 cc. of a hundredth-normal iodin increase, a blank on a clean filter paper giving 0.8 cc. of a hundredth-normal iodin.

E. R. Lyman: The chief difficulty seems to be incomplete precipitation with hydrogen sulphid. Out of eleven precipitations, three were incomplete, one of which was completed by a second precipitation. The manner of neutralizing and adjusting the acidity before precipitation should be specified more exactly. The volumetric method is more expeditious and satisfactory when the details are familiar. Method 3 seems preferable from present experience.

H. M. Miller: Sample 1 was unusually difficult to digest. Method 2 is far superior to Method 3. The latter is a modification of Lowenthal's method which specifies "for chloride or bromide solutions of tin." With such solutions excellent results were obtained, but with sulphuric acid solutions the results are uniformly low and the filtrates show the presence of tin when tested with hydrogen sulphid.

H. Runkel: In three determinations by Method 1 the filtrate from the sulphid precipitate was neutralized and made about 2 per cent acid with sulphuric acid. More tin was precipitated in each case. In Method 1 the statement "add 100 cc. of concentrated ammonia" should be changed to "make neutral to litmus with ammonia and add enough acid to make solution 2 per cent sulphuric acid." In Method 2 the statement "enough water is added to the flask to dilute the hydrochloric acid to about 30 to 40 per cent" should be changed for a statement of the total volume to which the solution is to be made.

W. W. Karnan: In Method 1 it is better if the sulphid precipitate stands overnight before filtering. The final precipitate sometimes passes through the filter with finely-divided sulphur and a second filtration is necessary.

H. R. Smith: Method 2 is easily feasible under ordinary laboratory conditions even with less than ten determinations to be made. Special attention should be paid to the starch indicator. If duplicate determinations do not agree it would seem that the higher result is more nearly the correct one.

E. L. P. Treuthardt: The results obtained on Sample 2 were not satisfactory but owing to lack of time the work was not repeated. In Method 3 large amounts of sodium sulphate precipitated in the neutral solution made the filtration, washing and dissolving of the precipitate difficult. The value of the iodin solution, when standardized for Method 3 against a hydrochloric acid solution of tin without asbestos, was practically the same as when standardized for Method 2 against a similar solution containing asbestos.

DISCUSSION BY THE REFEREE.

Method 1 at times gives unaccountably erratic results. In view of the fact that the four results marked "1" are so very low as compared with the rest, it is believed justifiable to exclude them from the averages used for comparing the accuracy of the methods. From a comparison of the averages, it is seen that Methods 1 and 2 give better results than Method 3. The table shows that the results obtained on Sample 1 are much more accurate than those obtained on Sample 2. This may be due to the elimination of sampling error in Sample 1, to the lower tin content of the same, or to the difference in chemical action of meat and sugar compounds during the process of analysis. The tin content of Sample 2 is three times that of Sample 1, but the average of the actual and percentage errors of determinations on the former are much more than three times those obtained on the latter. On Sample 1 the individual results show a variation both above and below the true value; by Method 1, eight results are above and seven below; by Method 2, seven results are above and four below; and by Method 3, two results are above and five below. On Sample 2 all results are lower than the true value. The number of results having a variation of ±1.0 mg. (10 per cent) in Sample 1 is:

Method 1, 12 out of 15, or 80 per cent
Method 2, 9 out of 11, or 82 per cent
Method 3, 5 out of 7, or 71 per cent

Omitting the two low results in Method 1 gives 12 out of 13 or 92 per cent. Those having a variation of ±3.0 mg. per kilo (10 per cent) in Sample 2 are:

Method 1, 10 out of 16, or 63 per cent
Method 2, 9 out of 13, or 69 per cent
Method 3, 4 out of 13, or 31 per cent

Omitting the two low results in Method 1 gives 10 out of 14 or 71 per cent.

With the exception of the occasional low results noted, the gravimetric method gives good results. It would seem in some cases that the proper conditions have not been observed. The chief trouble seems incomplete precipitation of tin as sulphid, due to too great acidity of the solution. It is not advisable to recommend the adoption of this method as provisional at present, but further work should be done with it with that end in view. The directions should be amended so as to make the condition of precipitation by hydrogen sulphid more definite. Another source of error is in the ignition of the precipitate. The stannic sulphid should be dry and should be very gently ignited at the start with a good oxidizing flame.

Baker's volumetric method gives results which are good after its details have been mastered, and is considered by most of the collaborators as better than the gravimetric method. It is not only advantageous as

a routine method, but is preferred by some even when small numbers of determinations are to be made. After the conditions for precipitation of stannic sulphid have been studied, it is believed that better results will be obtained by this method. As suggested by Mr. Runkel, the statement of dilution to the proper acid strength for reduction of tin in the flasks should be made more definite. With further work on the method as amended, it is hoped that results will be obtained which will allow of the recommendation of this method for adoption as provisional.

Method 3 is not yet in such form as to give good results. Under the conditions given, the tin is not all precipitated, the precipitate is not entirely dissolved in the flask, and the large amount of salts formed interfere with the operation. Further work with this method is recommended, however—the method seems promising but the details have not been worked out. H. M. Miller has recently done some work in this line and his comments should be noted.

RECOMMENDATIONS.

It is recommended—

(1) That the methods for the determination of lead in baking powder and baking powder materials be made the subject of further study, with the coöperation, if possible, of the associate referee on baking powder.

(2) That further study be made on the Gutzeit determination for arsenic, as carried on this year, especially as to the proper strength of acid to be used.

(3) That a study of some modification of the Marsh method for determination of arsenic be made.

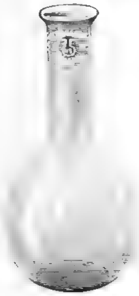
(4) That the gravimetric tin method and Baker's volumetric tin method be studied further with a view to their adoption as provisional. Especial attention in this connection should be given to the proper conditions of precipitating tin by hydrogen sulphid.

(5) That the volumetric tin method of Alexander, Bloomberg and Lourie be studied further.

(6) That the methods for the determination of copper, zinc, nickel, and aluminum in food products be made the subject of study by this association as soon as possible.

Adjourned at 5.30 p.m. for the day.

INDEX TO PROCEEDINGS OF THE THIRTIETH ANNUAL CONVENTION, 1913, AND TO THE FIRST TWO DAYS OF THE THIRTY-FIRST ANNUAL CONVENTION, 1914.



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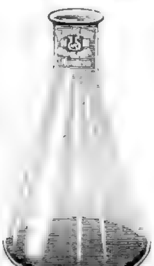

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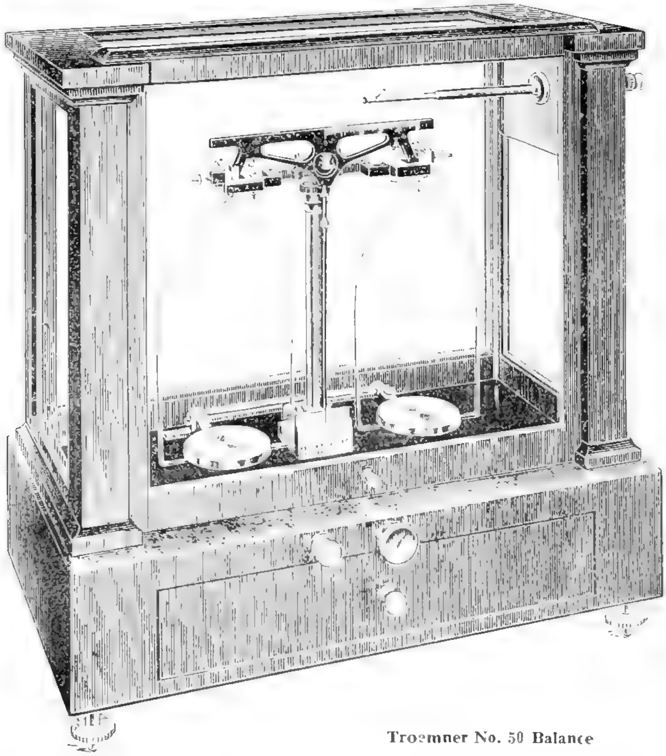

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